APTD-1071

PB 217 106

AIR POLLUTION

FROM

NITRATION PROCESSES

TASK ORDER NO. 22

CONTRACT NO. CPA 70-1

MARCH 31, 1972

PREPARED FOR

OFFICE OF AIR PROGRAMS

ENVIRONMENTAL PROTECTION AGENCY

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CINCINNATI, OHIO

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16. Abstracts: Using 1970 as the key year, those compounds which had a production of over 1 million pounds utilizing nitric acid or its oxides were studied. These compounds, their formulas, their 1970 production, and the amount of nitric acid utilized in their production are listed. The processes employed for the production of the 14 most important nitro products were surveyed. The study identifies the air pollutants from 15 selected major nitration processes, estimates the present and future quantities of pollutants, evaluates the applicability of control devices presently used in nitric acid production for controlling the air pollutants from the nitration processes, and recommends research and development objectives for the monitoring and controlling of these air pollutants. Adequate instrumentation for process control of nitro processes and for the utilization of pollution control devices is currently applied for process plants. At a cost of 4 cents per pound, the recovery of nitric acid and the oxides of nitrogen (NO_x) can be economically done.

17. Key Words and Document Analysis. 17a. Descriptors

Air pollution
Chemical industry
Nitric acid
Nitrogen oxides
Exhaust emissions
Air pollution control equipment
Instruments
Expenses

17b. Identifiers/Open-Ended Terms

17c. COSATI Field/Group 13B

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SECTION I - INTRODUCTION

A. SCOPE OF STUDY

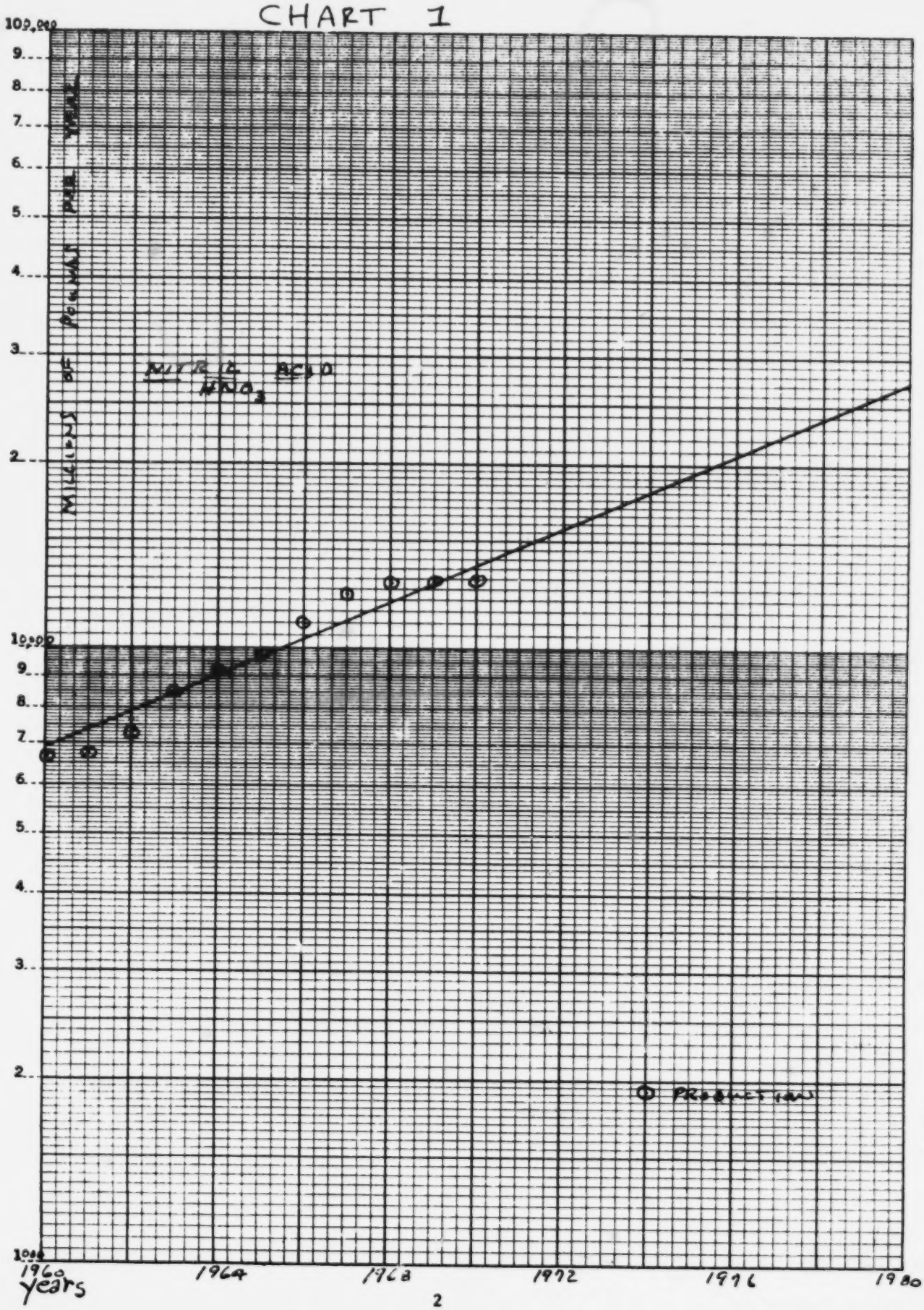
During the Sixties, the production of nitric acid approximately doubled, from 6.6 to 12.9 billion pounds. For the Seventies, the production is expected to double again, with the making of 25 billion pounds per year by 1980. Chart 1 shows a plot of the nitric acid production data.

Using 1970 as the key year, those compounds which had a production of over 1 million pounds utilizing nitric acid or its oxides were selected as important nitration compounds, and these were studied in this report. Table 1 lists these compounds, their formulas, their 1970 production, and the amount of nitric acid utilized in their production. The listings of this table account for about 95 percent of the nitric acid uses. The remaining 5 percent of the nitric acid production is used to make minor nitration compounds and industrial explosives. Over 75 percent of the nitric acid production is used to produce ammonium nitrate, while another 9 percent is used to make adipic acid. The remaining uses of nitric acid are small.

Probably because of the color of nitric oxides' fumes, nitration processes have long been considered to have the potential for atmospheric pollution. Therefore, a survey of the processes employed for the production of the 14 most important nitro products was undertaken.

Processes and production data were accumulated using forms and techniques developed under Environmental Protection Agency, Office of Air Programs, Contract 70-1, Task Order No. 4. An explanation of the system is shown in Section II of this report.

CHART 1



K&E SEMI-LOGARITHMIC 46 4853
2 CYCLES X 60 DIVISIONS
KEUFFEL & ESSER CO.

This study covers the pollution of atmospheric air by processes which utilize nitric acid. It does not cover air pollution by nitric acid production, or the nitric acid treatment by the fertilizer industry of phosphate rock. The study identifies the air pollutants from 15 selected major nitration processes, estimates the present and future quantities of pollutants, evaluates the applicability of control devices presently used in nitric acid production for controlling the air pollutants from the nitration processes, and recommends research and development objectives for the monitoring and controlling of these air pollutants.

The tariff commission does not publish production figures on explosives. The Bureau of Mines, however, compiles statistics on the consumption of industrial explosives and their figures indicate a 6 percent annual growth rate. It is estimated for 1970 that the consumption of industrial explosives was over 2 billion pounds. The important nitration compounds classified as explosives are:

Ammonium nitrate
Nitroglycerine
Trinitrotoluene
Nitrocellulose
Dinitrotoluene
Dinitrobenzene

The main use of ammonium nitrate is as a fertilizer. About 1.5 million pounds of nitrocellulose per year are used in plastics. About 300 million pounds of dinitrotoluene per year are used in polyurethane production; this use has been included in Table 1. Also, dinitrobenzene is an important intermediate. An attempt has been made in the study to include all typical nitric acid reactions.

TABLE 1 - LIST OF MAJOR NITRATION COMPOUNDS

Compound	Formula	1970 MPPY	As HNO_3 MPPY	Percent HNO_3 Production	Total Compound Production
Ammonium Nitrate	NH_4NO_3	12,400	9,760	75.6	
Adipic Acid	$C_6H_{10}O_4$	1,300	1,200	9.3	
Terephthalic Acid	$C_8O_4H_6$	400(1)	230	1.8	1,300
Acrylonitrile	C_3H_3N	100(1)	200	1.5	1,037
Nitrobenzene	$C_6H_5NO_2$	515	278	2.15	
Dinitrotoluene	$C_7H_6(NO_2)_2$	290	223	1.73	
Nitrochlorobenzene	$C_6H_4ClNO_2$	100	45	0.35	
Oxalic Acid	$C_2H_2O_4$	2(1)	15	0.12	23
Nitroparaffins	RNO_2	20	16	0.12	
Nitrocellulose	$C_6H_7N_3O_{11}$	---	---	---	No Data
Nitroglycerine	$C_3H_5N_3O_9$	65	65	0.50	Industrial only
Trinitrotoluene	$C_7H_5N_3O_6$	23	23	0.18	Industrial only
Potassium Nitrate	KNO_3	126	117	0.90	
Sodium Nitrite	$NaNO_2$	100	96	0.74	
HNO_3 Accounted For			12,268	95	
Nitric Acid	HNO_3	12,920			

(1) By nitro processes

The principles discussed here may then be applied to any reactions that become significant in the future.

Areas outside the scope of this study are:

a. Oxides of nitrogen from fuel burning.

b. Oxides of nitrogen from explosives.

c. Process upsets; for example, the dumping of batches of explosives into a drown tank.

d. Minor explosives such as urea nitrate or nitrostarch.

SECTION II - MANUFACTURING TECHNOLOGY

A. CLASSES OF PROCESSES

Nitric acid has two important chemical properties. First, nitric acid can nitrate a material. For example:

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3 \quad \text{or}$$

$$C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$$

Second, nitric acid or oxides of nitrogen can oxidize a material. For example:

$$C_6H_4(CH_3)_2 + 4HNO_3 \longrightarrow C_6H_4(COOH)_2 + 4H_2O + 4NO$$

Using various physical conditions and these two chemical properties, the processes involving nitric acid have been classified into four types of reactions, namely:

1. Liquid phase nitrations at temperatures below 100C and at atmospheric pressures.

2. Vapor phase nitrations at temperatures over 200C and at pressures of over 50 psig.

3. Liquid phase nitric acid oxidations at temperatures below 100C.

4. Nitric oxide oxidations at atmospheric pressure.

Table 2 summarizes the classifications.

B. DISCUSSION OF INDUSTRIES, PROCESSES, PRODUCTS, SOURCES AND EMISSIONS

Introduction. Production of the 14 major nitro compounds is carried out using 15 nitro processes. Three of the nitro compounds can be made by alternate processes. The alternate processes do not use nitric acid or its oxides and,

TABLE 2 - CLASSIFICATION OF NITRATION PRODUCT/PROCESSES

Process	Product	1970 Production Million Pounds	Reaction Phase	Temperature, C	Pressure	Process Classification	Total Emissions Millions of Pounds Per Year	Emission Factors: Nox	Particulate	Others
Nitration of Ammonia	Solution of Ammonium Nitrate	3,360(3)	Liquid	50 - 80	Atm	1	0	--	--	--
Nitration of Ammonia	Prill of Ammonium Nitrate	7,900	Liquid	80 - 80	Atm	1	3.6	--	0.90	--
Nitration of Ammonia	Granules of Ammonium Nitrate	1,160	Vapor	230 - 240	30 psig	2	3.1	1.3	1.	0.2 as SO_2
Nitric Acid Oxidation of Cyclohexanol	Adipic Acid	1,300	Liquid	70 - 100	50 - 250 psig	3	9.0	12	1.0	--
Nitric Acid Oxidation of Paraxylene	Terephthalic Acid	200(2) (1,300 total)	Liquid	(Est) 100	Atm	3	2.8	13	1.0	--
Nitric Oxide Oxidation of Propylene	Acrylonitrile	100(2) (1,000 total)	Vapor	400 - 500	Atm	4	0.45	--	--	0.2 as HCN
Nitration of Benzene	Nitrobenzene	1,5	Liquid	50 - 60	Atm	1	0.6	0.2	--	18.0 in Cake
Nitration of Toluene	Dinitrotoluene	290	Liquid	75 - 85	Atm	1	1.039	0.27	--	--
Nitration of Chlorobenzene	Nitrochloro-benzenes	100	Liquid	70 - 90	Atm	1	0.41	0.2	--	3.2 as C_6H_5Cl
Nitric Acid Oxidation of Glucose	Oxalic Acid	2(2) (23 total)	Liquid	50	Atm	1	2.0+6	4.3	1.0	--
Nitration of Paraffins	Nitroparaffins	21	Vapor	350 - 450	125 - 175 psig	1	0.011	1.3	--	--
Nitric Acid Oxidation of Potassium Chloride	Potassium Nitrate and Chlorine	126	Liquid	(Est) 100	20 psig	3	0.02	0.2	0.9	0.001 as HCl
Nitric Oxide Oxidation of Sodium Carbonate	Sodium Nitrate	100	Liquid	(Est) 100	Atm	4	0.018	--	1.0	--
Nitration of Glycerine	Nitroglycerine	(65)(2)	Liquid	15	Atm	1	0.063	1.0	--	--
Nitration of Toluene	Trinitrotoluene	(23)(2)	Liquid	50	Atm	1	0.1	17	--	47 as SO_2
Nitration of Cellulose	Nitrocellulose	--	Liquid	30	Atm	1	--	31	--	47 as SO_2

(1) By this process
(2) Industrial explosives only
(3) Part of Prill process

therefore, have not been studied. The 14 compounds have been classified into four SIC Industry numbers as established by the Department of Commerce. The Department of Commerce publishes, on a routine basis, SIC compound production data.

In an earlier EPA-OAP project (Contract No. CPA 70-1), a computer program was set up to catalog and record air pollution sources. The data of this study have been organized on the basis of this program.

For the computer program, a system of nomenclature involving the basic categories of "industry," "process," and "source" was developed, using definitions for each category which were believed applicable to all industries. A subcategory "product" was created to facilitate handling of data in those industries where many polluting processes, sometimes producing identical products, are found. It is anticipated that this subcategory will be used only for the more complex industry groups. The definition for each category follows:

Industry. An industry, as defined for cataloging purposes, will correspond with headings in the SIC Manual. That manual is subdivided into "Major Group," each with a unique two-digit numerical code, and subcategories within each Major Group called "Group Number," each of which has a number of designated subgroups called "Industry Number." For example, Major Group 28 "Chemicals and Allied Products" includes the Group Number 281 "Industrial Inorganic and Organic Chemicals," which is further subdivided into Industry Number groups such as 2818 - "Industrial Organic Chemicals Not Elsewhere Classified" and 2819 - "Industrial Inorganic Chemicals Not Elsewhere Classified." Under each four-digit industry number a listing of included products is shown.

Process. As the term is used here, it includes processes in which a single product is prepared by a specific procedure involving chemical change or change in state, and unit operations where a class of products is manufactured by use of essentially identical equipment and operations. For example, the product sulfuric acid is produced both by the chamber process and by the contact process, and both would be included as processes. Also included would be the unit operations such as galvanizing, degreasing, and other operations used in the manufacture of many fabricated metal products. All processes fall within some industry category as previously defined.

Product. As the term is used for this study, a product is a subcategory useful for relating process to industry in the SIC codes as described above. Also, it is useful as a subdivision for certain industries, such as 2818 - Industrial Organic Chemicals, where a large number of processes are included despite the fact that the smallest subdivision in the SIC Manual is used for definition of the industry.

Source. As defined for this study, a source is a piece of equipment, essential to the operation of a process, from which air pollution emissions occur unless the emissions are prevented by application of pollution control technology. By contrast, a piece of equipment installed for the primary purpose of minimizing air pollution emissions is considered control equipment for a source. Thus, a specific type of equipment, such as a scrubber, may be classifiable as a source or as control equipment, depending on its role in the process.

Data Limitations. Complete and valid data were not always available. Therefore, it was necessary in some instances to estimate emission factors, source control factors, processes, and production levels. To qualify the validity of the data, the following code was used:

A = Valid data. The result of census or experiment.

B = Estimated data. Estimate based on limited census or experimental data.

C = Estimated data. Estimate based on little or no census or experimental data.

Emission factors which were used are an average factor for all sources, and the source factor (estimated percent of existing sources which are controlled) is a national average. Application of such numbers to individual plants or to a small number of plants in a given geographical area could yield erroneous results.

Product Discussion. Under each of the 14 nitro products, the various methods of producing the compound are discussed. Production and capacity data from 1960 are also shown, along with the major uses. A 1980 production forecast is included.

Process Discussion. Each process is described in detail covering feed preparation, reaction conditions, product purification, recycle systems, raw materials, by-products, and sources of air pollution. A process flow sheet has also been included.

Process Data Tabulation. On the attached form, AQCR means Air Quality Control Region, and the capacity is in millions of pounds per year.

Source Data Tabulation. On this form, the emission factors are in pounds per ton of product, the efficiency factor shows the portion of pollutant retained in the control device as a decimal, and the source factor is the portion of the plants equipped with control devices, expressed as a decimal.

C. CATALOG OF SOURCES

1. Cyclic Intermediates - SIC Industry No. 2815

Establishments primarily engaged in manufacturing cyclic organic intermediates. Important products of this industry include:

Derivatives of benzene, toluene, naphthalene
Synthetic organic dyes
Synthetic organic pigments
Cyclic crudes

Some of the nitro cyclic intermediates are:

Nitroaniline
Nitrobenzene
Nitro dyes
Nitrophenols

This study includes, for Industry No. 2815, nitrobenzene, terephthalic acid, dinitrotoluene and nitrochlorobenzene. The production of these four products consumes about 6 percent of the nitric acid production.

PROCESS DATA TABULATION

SH____OF____

SIC. NO.	INDUSTRY	PRODUCT

DATE:	PROCESS

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X					
PRODUCT : COLS. 5-8	X					
PROCESS : COLS. 9-13						

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25 36	COMPANY 37 49	X 50 51	CAPACITY 52 55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
DATE PREPARED	PROCESS	SOURCE	SIC. NO. : COLS. 1-4 [X]
			PRODUCT : COLS. 5-8 [X]
			PROCESS : COLS. 9-13
			SOURCE : COLS. 14-17 [X]

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q

COMPUTER CODE NOS.

PNO 18–20	CNO 21–23	UNCON EMISS 24–30	Q 31	OEF 32–35	Q 36	SCF 37–40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Nitrobenzene

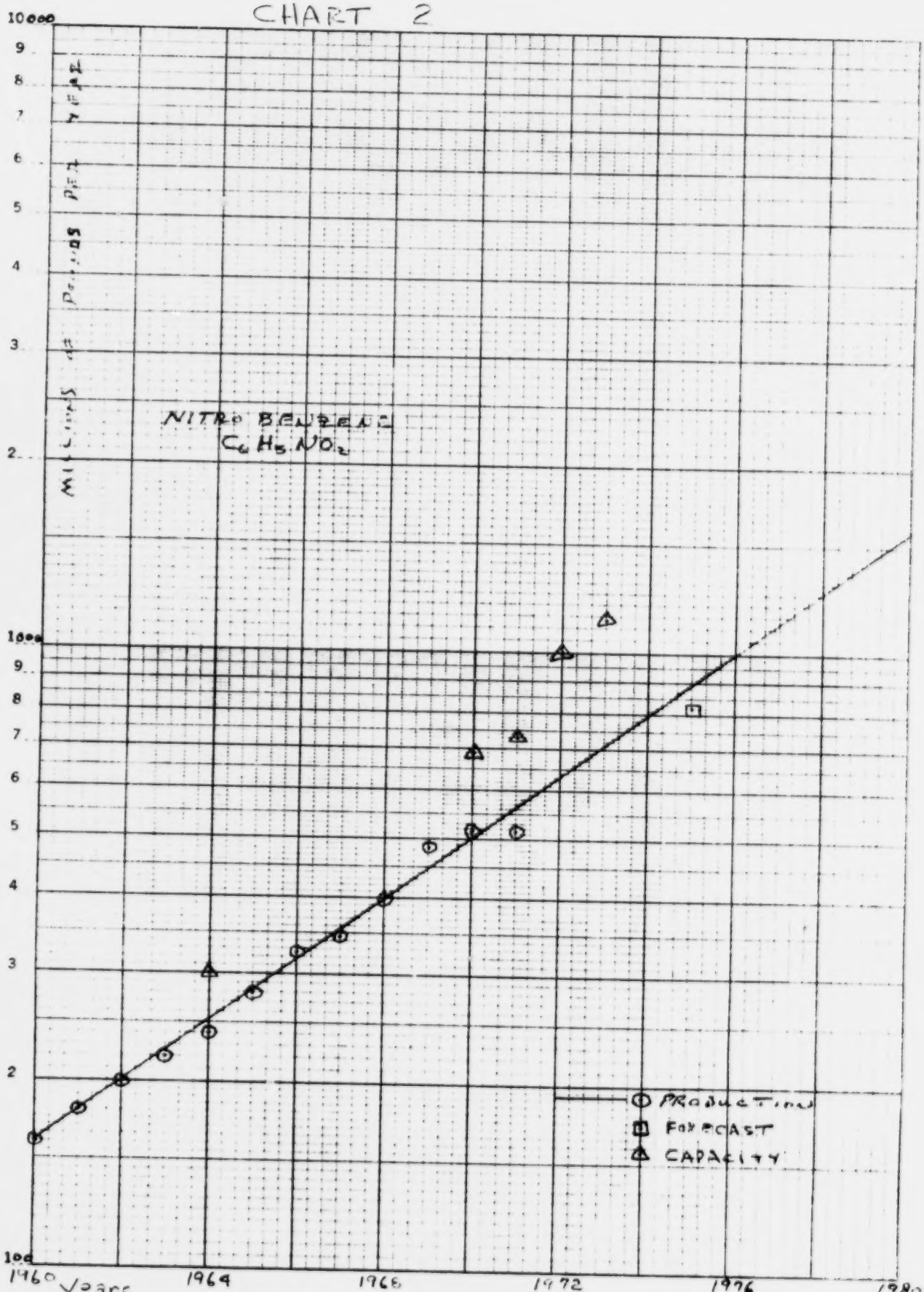
Nitrobenzene is produced by reacting benzene and nitric acid in the liquid phase,

$$C_6H_6 + HONO_2 \longrightarrow C_6H_5NO_2 + H_2O$$

In the Sixties, the annual growth rate was 12 percent. For the Seventies, an annual growth rate of 10 percent is expected. Chart 2 shows a plot of the production data for nitrobenzene.

About 97 percent of the nitrobenzene production is used to make aniline.

CHART 2


Millions of Pounds per Year
NITRO BENZENE
$C_6H_5NO_2$
10000
9
8
7
6
5
4
3
2
1000
9
8
7
6
5
4
3
2
100
1960 years
1964
1968
1972
1976
1980
PRODUCTION
FORECAST
CAPACITY

Process: Nitration of Benzene to Nitrobenzene

a. Feed Preparation

A mixed acid is used in the reactor. This acid has a composition of 53 percent H_2SO_4, 39 percent HNO_3, and 8 percent H_2O. The mixed acid is prepared by mixing 93 percent H_2SO_4, 97 percent HNO_3 and 50 to 60 percent HNO_3. The benzene requires no feed preparation.

b. Reaction Conditions

The reaction is carried out either in batches or continuously.

For batch operation, the kettles are sized for 1000 to 1500 pound quantities of benzene, and are equipped with agitators. They are jacketed and also have internal coils for cooling.

The reaction cycle requires two to four hours. The benzene is charged to the reactor along with a heel of spent acid. The mixed acid is added slowly below the surface of the benzene. The temperature is maintained at 50 to 55C, but is allowed to rise to 90C toward the end of the reaction to promote complete reaction.

The reactor vents to an absorber.

An emergency drown tank is provided, located below the reactor. In case of a runaway reaction in the reactor, the batch is dumped to the drown tank, which contains water to kill the reaction.

When the reaction is complete, the reactor batch is transferred to a separato. tank. The overall process yield from benzene is 95 to 98 percent.

c. Product Purification

In the separator tank, the crude nitrobenzene separates from the spent acid by gravity. The spent acid either goes to provide a heel for the next reactor batch or to acid concentration. There is a loss of 0.5 percent yield of nitrobenzene in the spent acid.

If the nitrobenzene is to be used to make aniline (most of the nitrobenzene which is made is so used), the crude nitrobenzene from the separator is transferred to the aniline process.

If a nitrobenzene of high purity is desired, the crude nitrobenzene is transferred to a washer where it is washed with water and sodium carbonate solution to remove residual spent acid. The crude is then distilled to obtain the desired pure nitrobenzene product. The residuals from distillation are wastes.

d. Recycle Systems

The vents from the reactor go to an absorber, where any NO_x is oxidized with air and absorbed in water to produce nitric acid. The unreacted air is vented. The acid stream goes to acid concentration.

In the acid concentration system, spent acid and acid from the reactor vent absorber first go to the top of a denitrating tower, which is heated with steam. As the liquids flow down through the tower, rising vapors strip all HNO_3 and oxides of nitrogen. The water in the feed remains with the sulfuric acid, which is drawn off the bottom of the tower. The overhead gases go to the bleacher. The dilute sulfuric acid goes to a sulfuric acid concentrator.

In the bleacher the vent gases are oxidized with air and pass through a reflux condenser where any HNO_3 present condenses and drops back to the bleacher. Nitric acid with a concentration of 97 percent is drawn off from the bottom of the bleacher, and goes to the mixed acid system.

The off gases from the reflux condenser go to an absorber column, where additional oxidation takes place and the oxides of nitrogen are absorbed in nitric acid and water to produce nitric acid. The nitric acid from the bottom of the column is recycled to the denitrating column. The air from the absorber is vented.

The sulfuric acid from the bottom of the denitrating column goes to a sulfuric acid concentrator where the acid is concentrated to 93 percent sulfuric acid. The sulfuric acid produced goes to the mixed acid system. The water removal is a waste.

e. Raw Materials

The major raw materials are benzene and 50 to 60 percent nitric acid. Other raw materials are 93 percent sulfuric acid to make up for process losses and sodium carbonate which is used in the washer.

f. By-products

There are no by-products.

g. Sources of Air Pollutants

There are two sources of air pollution. These are the absorber on the reactor vents and the absorber on the acid concentration system. Both of these vent air and unabsorbed oxides of nitrogen.

PR 109

FLOW DIAGRAM
NITROBENZENE MANUFACTURE

Job EPA

Location

Subject NITRATION STUDY

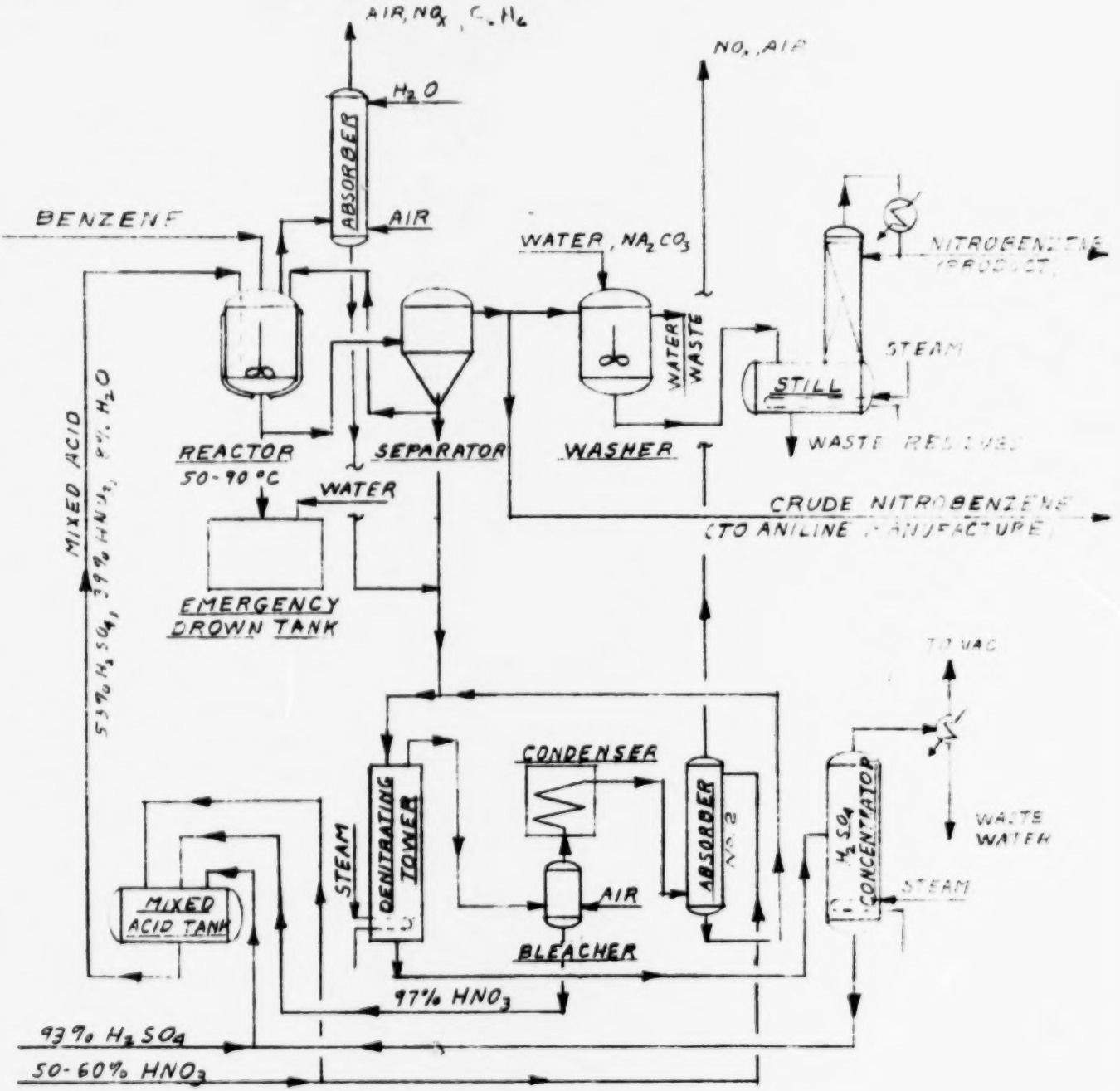
PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

File No 334 Sheet No

Checked by Date

Computed by S.N.T. Date 6-21-71

PROCESS: NITRATION OF BENZENE



Q-2

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2815	CYCLIC INTERMEDIATES	NITRO BENZENE

DATE:	PROCESS
11-15-71	NITRATION OF BENZENE

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	1	5
PRODUCT : COLS. 5-8	X		1	3	5
PROCESS : COLS. 9-13				5	3

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
13	AMER. CYAN.	BROWNS BROOK, NJ	A	85	A
10	AMER. CYAN.	WILLOW ISLAND, WV	A	60	A
15	DUPONT	GIBBSTOWN, NJ	A	225	A
68	FIRST CHEMICAL	PASCAGOULA, MS	A	95	A
10	MOBAY	NEW MARTINSVILLE, WV	A	95	A
26	MONSANTO	MONSANTO, IL	B	10	A
53	PUBLICON	GEISMAR, LA	A	65	A
33	ALLIED	MOUNDSVILLE, WV	A	55	A

COMPUTER CODE NOS.

AQCR 19	STATE 22 23 24 25	CITY 26	COMPANY 37	49	X 50	CAPACITY 51 52	55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS.

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2815	CYCLIC INTERMEDIATES	NITRO BENZENE	SIC. NO. : COLS. 1-4 — X 2815
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8 — X 135
11/15/	NITRATION OF BENZENE	ABSORBER (REACTOR)	PROCESS : COLS. 9-13 — 53
			SOURCE : COLS. 14-17 — X 1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
C_6H_6	16.6	C
$C_6H_5NO_2$	NIL	B
NO_x	0.18	B

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				
"				
"				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	24 UNCON EMISS 30	Q 31	32 CEF 35	Q 36	37 SCF 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2815	CYCLIC INTERMEDIATES	NITRO BENZENE	SIC. NO. : COLS. 1-4 — X 2 8 1 5
DATE PREPARED	PROCESS NITRATION BENZENE	SOURCE ABSORBER (No. 2)	PRODUCT : COLS. 5-8 — X 1 3 5
			PROCESS : COLS. 9-13 — 5 3
			SOURCE : COLS. 14-17 — X 5

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	0.32	B

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNC 18 20	CNO 21 23	24 UNCON EMISS 30	Q 31	32 CEF 36	Q 36	37 SCF 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Terephthalic Acid

Terephthalic acid is made by oxidizing P-xylene. About 30 percent of the terephthalic acid production is oxidized by nitric acid,

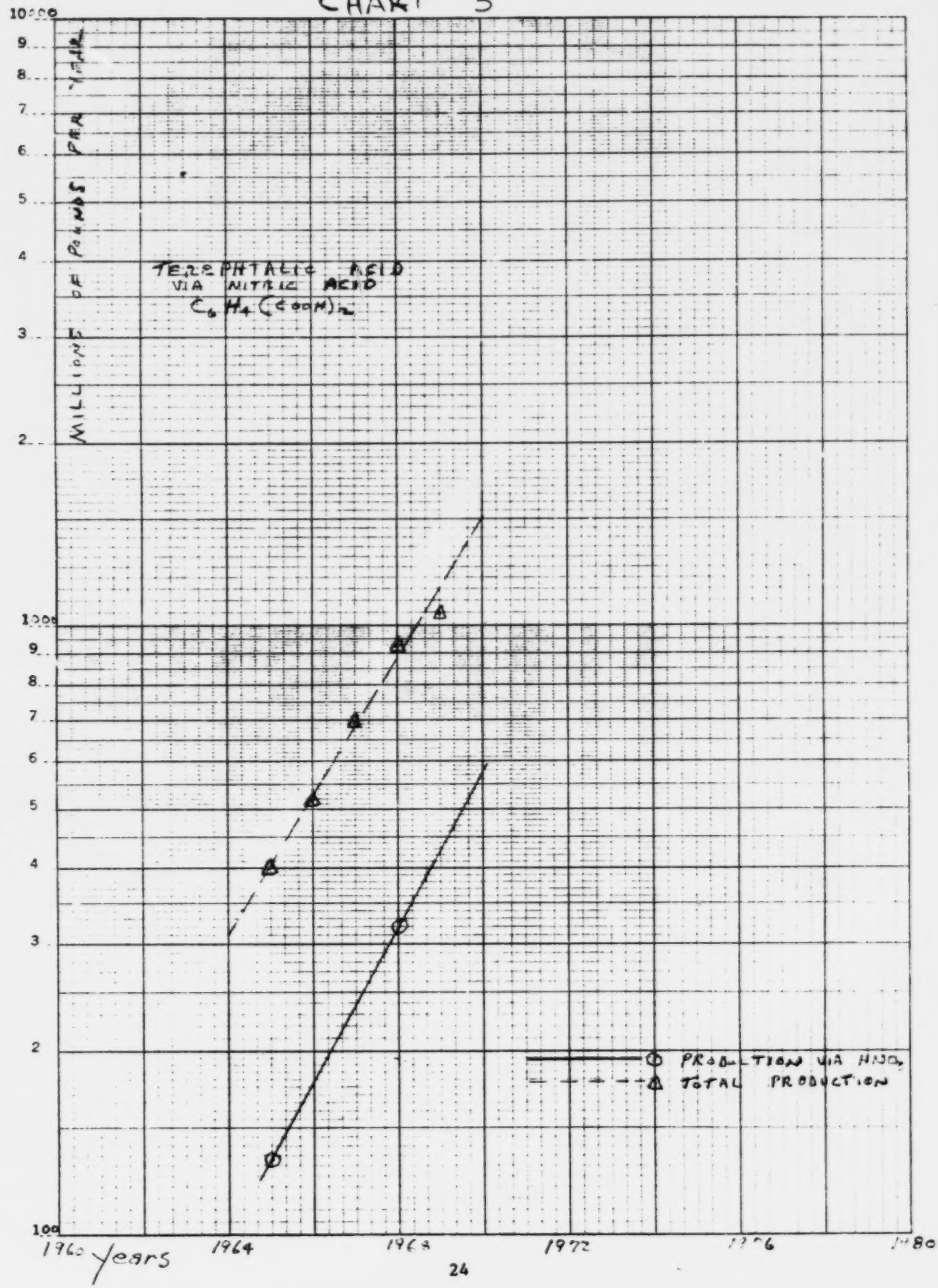
$$C_6H_4(CH_3)_2 + 4HNO_3 \longrightarrow C_6H_4(COOH)_2 + 2H_2O + 4NO$$

The remaining production is made by air oxidation,

$$C_6H_4(CH_3)_2 + 3O_2 \longrightarrow C_6H_4(COOH)_2 + 2H_2O$$

In 1970, about 1-1/2 billion pounds of terephthalic acid were produced. Dacron is polyethylene terephthalate. An annual growth rate of about 30 percent is expected to continue. See Chart 3.

CHART 3


MILLION POUNDS PER YEAR
TEREPHTHALIC ACID
VIA NITRIC ACID
$C_6H_4(COOH)_2$
PRODUCTION VIA HNO_3
TOTAL PRODUCTION
1960 years
1964
1968
1972
1976
1980

Process: Oxidation of P-xylene to Terephthalic Acid

a. Feed Preparation

No feed preparation is required.

b. Reaction Conditions

The reaction is a liquid phase reaction in which paraxylene and nitric acid (40 to 50 percent) are mixed,and react. (The operating temperature and pressure have not been published.) Terephthalic acid crystallizes out of the solution during the reaction. The slurry formed in the reactor goes to a filter. NO gas, which is generated by the reaction, goes to recovery.

c. Product Purification

When the slurry from the reaction step is filtered, the mother liquor (consisting of water and unreacted nitric acid) goes to the NO recovery system.

The cake from filtration is dried to become the terephthalic acid product for feed to a Dacron process.

d. Recycle Systems

The NO off gas from the reactor is fed to an oxidizer column, where it is mixed with air. This oxidizes some of the NO to NO_2. The mother liquor from filtration is fed to the top of the oxidizer column and absorbs the oxides of nitrogen to form a dilute nitric acid solution. The spent air from the oxidizer column is vented.

The dilute nitric acid produced in the oxidizer column is concentrated to 40 to 50 percent nitric acid and recycled to the reactor.

e. Raw Materials

Two raw materials are used. Paraxylene is the chief raw material. Some nitric acid (40 to 50 percent) is required to make up for process losses.

f. By-products

There are no by-products.

g. Air Pollution Sources

There are two sources of air pollution. The vent from the NO oxidizer column will contain air and unabsorbed oxides of nitrogen. The dryer, if it uses air to pick up the moisture, will have a vent which contains air, moisture, and probably product particulates.

FLOW DIAGRAM

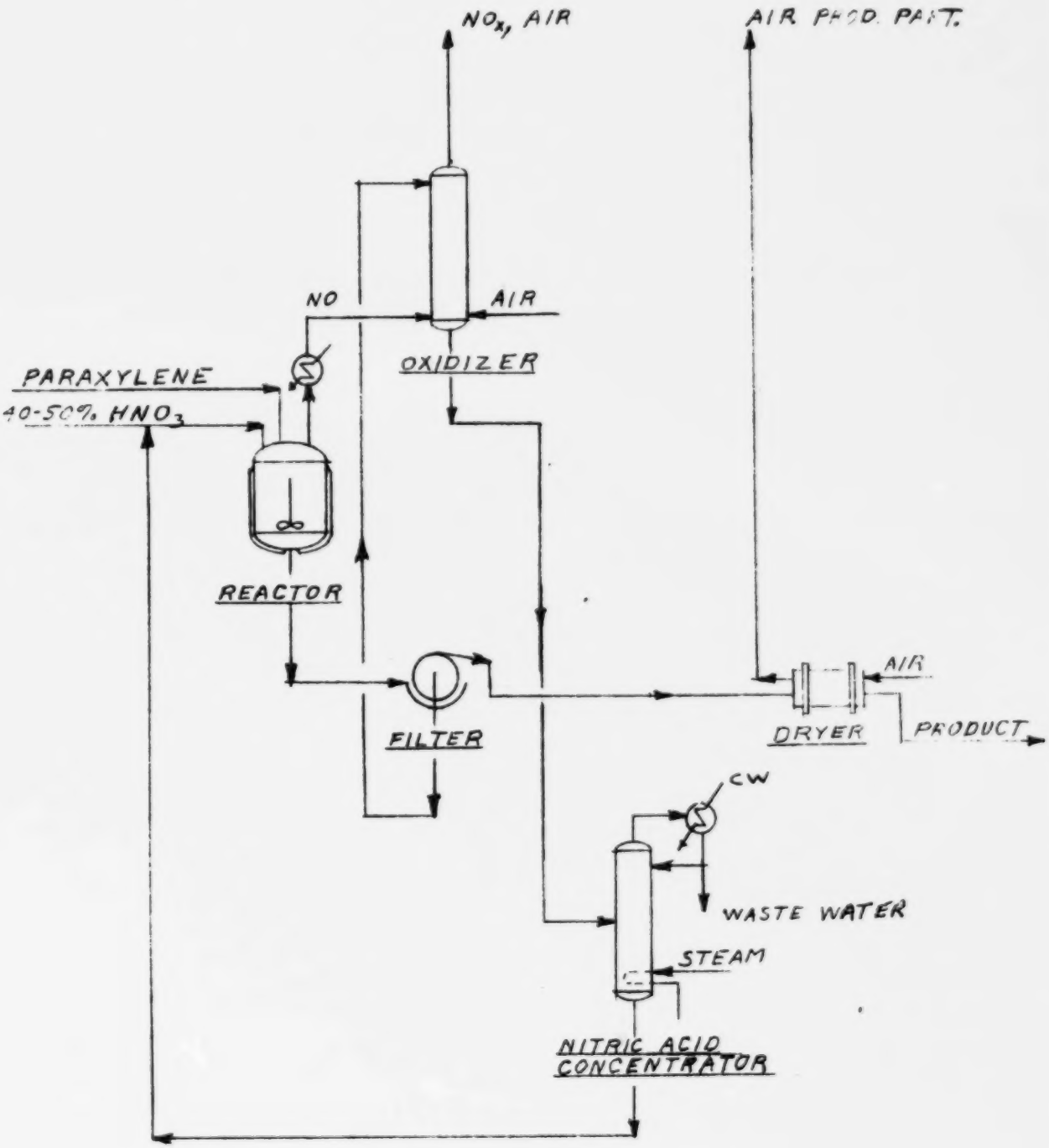
PR 109 TEREPHTHALIC ACID MANUFACTURE

Job EPA — PROCESSES RESEARCH, INC. — File No 3382 Sheet No

Location — INDUSTRIAL PLANNING AND RESEARCH — Checked by Date

Subject NITRATION STUDY — CINCINNATI NEW YORK — Computed by GNT Date 10-25-71

Process: NITRIC ACID OXIDATION OF PARAXYLENE



PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2818	IOC	TEREPHTHALIC ACID

DATE:	PROCESS
11-16-71	OXIDATION OF P-XYLENE

COMPUTER CODE NOS.

SIC. NO.	COLS. 1-4	X	2	8	1 8
PRODUCT	COLS 5-8	X		1	4 2
PROCESS	COLS. 9-13				6 0

PRODUCTION DATA

AOCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
15	DU PONT	GIBBSTOWN, NJ	A	120	C
131	EL PASO	ODESSA, TX	A		
120	DUPONT	OLD HICKORY, TN	A	20	B

COMPUTER CODE NOS.

AOCR 19	STATE 22 23 24	CITY 25	36	COMPANY 37	49	CAPACITY 50 51 52	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT
2818	IOC	TEREPHTHALIC ACID
DATE PREPARED	PROCESS	SOURCE
11-16-71	OXIDATION OF P-XYLENE	ABSORBER (OXIDIZER)

COMPUTER CODE NOS.

SIC NO.	COLS 1-4	X 2818
PRODUCT	COLS 5-8	X 1402
PROCESS	COLS 9-13	60
SOURCE	COLS 14-17	X 1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO	13	A

CONTROL DEVICE

TYPE	EFF FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23 24	UNCON EMISS 30	Q 31	CEF 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

2-12-2

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2818	IOC	TEREPHTHALIC ACID	SIC. NO. : COLS. 1-4 — X 2818
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8 — X 142
11-16-71	OXIDATION OF P-XYLENE	DRYER	PROCESS : COLS. 9-13 — 60
			SOURCE : COLS. 14-17 — X 11

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
PARTICULATES	1.8	B

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO 18	CNO 20 21	23 24	UNCON EMISS 30	Q 31	CEF 32	35	Q 36	SCF 37	40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Dinitrotoluene

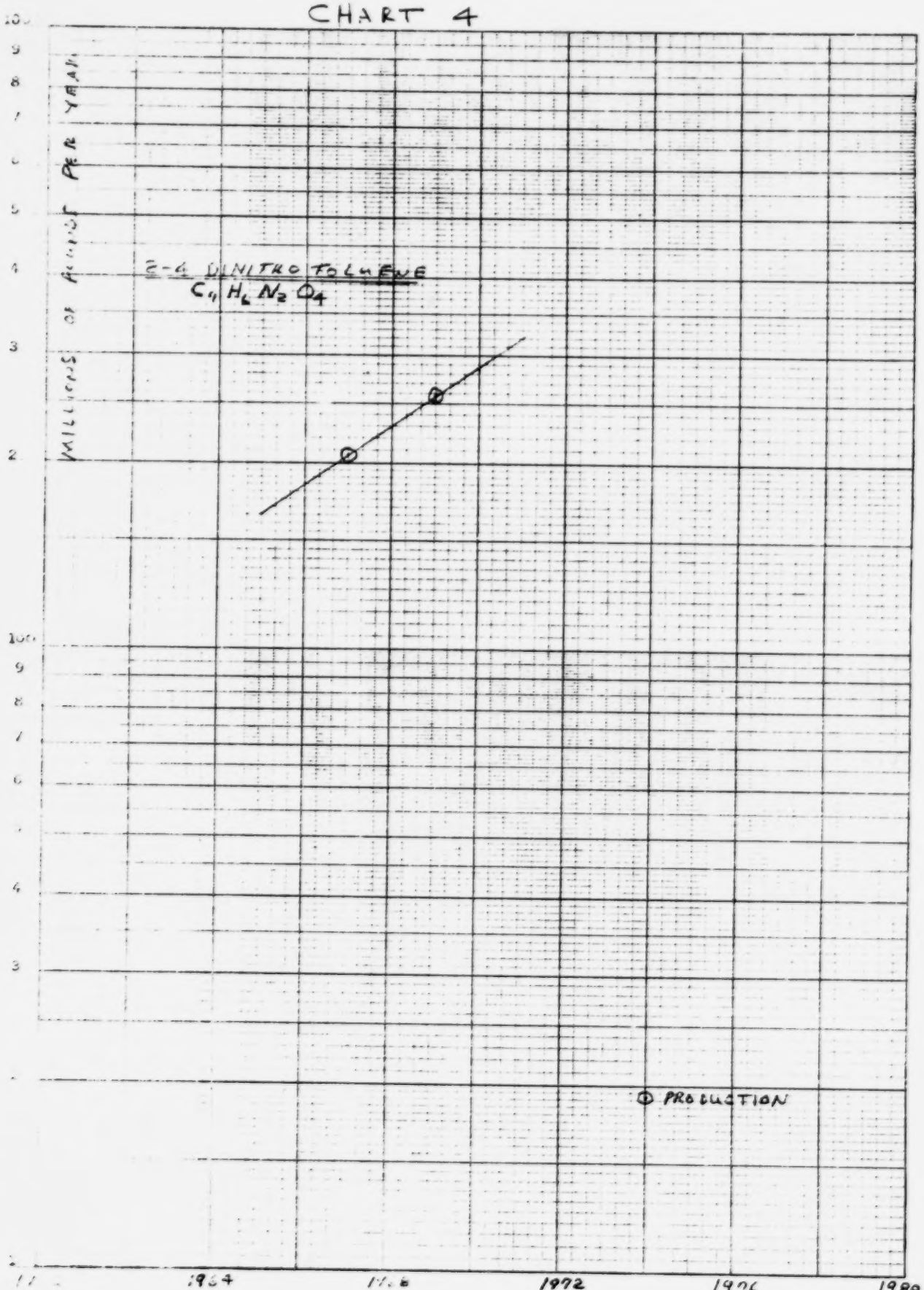
Dinitrotoluene is an explosive. It is mixed with NH_4NO_3 and acts as a promoter. Therefore, there is little production data on mono or dinitrotoluene. However, in the Sixties, dinitrotoluene has become an important industrial intermediate for the production of polyurethanes. In the late Sixties, some production data have been published on dinitrotoluene, as shown on Chart 4.

Dinitrotoluene is made by nitrating nitrotoluene,

$$C_6H_4CH_3NO_2 + HONO_2 \longrightarrow C_6H_3CH_3(NO_2)_2 + H_2O$$

An annual growth rate of about 20 to 25 percent is expected. Also, for nitrotoluene production, it should be noted that toluene nitrates easier than benzene.

CHART 4


MILLIONS OF POUNDS PER YEAR
2,4 DINITROTOLUENE
$C_7H_6N_2O_4$
10
9
8
7
6
5
4
3
2
100
9
8
7
6
4
3
1964
1968
1972
1976
1980
⊙ PRODUCTION

Process: Nitration of Nitrotoluene to Dinitrotoluene

a. Feed Preparation

This process uses a mixed acid with an approximate composition of 72 percent H_2SO_4, 17 percent HNO_3 and 11 percent H_2O. The mixed acid is prepared by mixing 50 to 60 percent HNO_3 with 93 percent H_2SO_4. The nitrotoluene requires no feed preparation.

b. Reaction Conditions

The process may be either batch or continuous. The same process steps are used for either process. For the continuous process, the reaction step consists of one or more reaction vessels in series, with all the feed going to the first vessel and with any subsequent vessels providing additional time for the reaction to go to completion. The reactors are provided with agitators and jackets or coils for cooling.

Mixed acid (as described under feed preparation), and either ortho or paranitrotoluene are fed separately and continuously as liquids to the reactor. A stoichiometric ratio of nitrotoluene to nitric acid in the mixed acid is used. The reaction is exothermic, and is controlled at 75 to 85C. The liquid product from the reactor overflows to the decanter. The reactors vent to an absorber. The yield is 96 percent.

c. Product Purification

The liquid product from the reaction step is separated in the decanter to give a spent acid layer and a crude 2,4-dinitrotoluene layer. The spent acid layer is recycled (see recycle systems).

The crude 2,4-dinitrotoluene is washed and neutralized continuously in a series of steps. In the Meissner process these steps are as follows. The crude is washed, with water and with the waste water from the second step washing, in a column in which both liquids flow upward concurrently. Air is fed to the bottom of the column, and flows upward with the liquids to provide agitation.

The liquids flow out the top of the column to a continuous decanter. The air vents to atmosphere from the top of the column. In the decanter the wash water separates out and is discarded. The organics layer is fed to a second stage column which operates in the same manner as the first column described above. The wash water consists of the waste water from the third washing step and a dilute solution of sodium bicarbonate which neutralizes any acids present. The liquids from this second column flow to a continuous decanter. The air is vented. In the decanter, a water layer separates from the organic layer and is fed to the first washing column. The organic layer is fed to a third stage of washing, which consists of a column and decanter similar to the other two stages. Water is used for washing. The organic stream from this stage is the product.

If orthonitrotoluene is used as the feed material, there will be some 2,6-dinitrotoluene present in the product. If a high purity 2,4-dinitrotoluene product is desired, it is obtained by distillation of the product from the third washing step.

d. Recycle Systems

Two recycle systems exist. The first system involves the spent acid from the reaction system. This acid is fed continuously to the spent acid

washer, where it is mixed with a continuous flow of fresh nitrotoluene. Any residual nitric acid in the spent acid reacts with the nitrotoluene to form 2,4-dinitrotoluene and to produce a spent acid that does not require denitrification. The spent acid and nitrotoluene are separated in a continuous decanter. The nitrotoluene layer becomes feed to the reaction step. The spent acid is fed to an H_2SO_4 concentrator, where the acid is concentrated to 93 percent H_2SO_4 for feed to the mixed acid system.

The second recycle system involves the absorber. The vents from the reactors go to the absorber, where any NO is oxidized and absorbed in water to produce nitric acid. The nitric acid is fed to the mixed acid system. The air is vented.

e. Raw Materials

The major raw materials are 50 to 60 percent nitric acid and either orthonitrotoluene or paranitrotoluene. Minor raw materials are 93 percent sulfuric acid to make up for process losses, and sodium bicarbonate used in the washing operations.

f. By-products

No by-products are produced.

g. Sources of Air Pollution

There are two sources of air pollution. One is the vent from the absorber, which will consist of air and any unabsorbed oxides of nitrogen. The second is the vents from the washers, which will be air saturated with water and 2,4-dinitrotoluene.

PR 109

FLOW DIAGRAM
2-4 DINITROTOLUENE MANUFACTURE

Job EPA

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

File No 3382 Sheet No

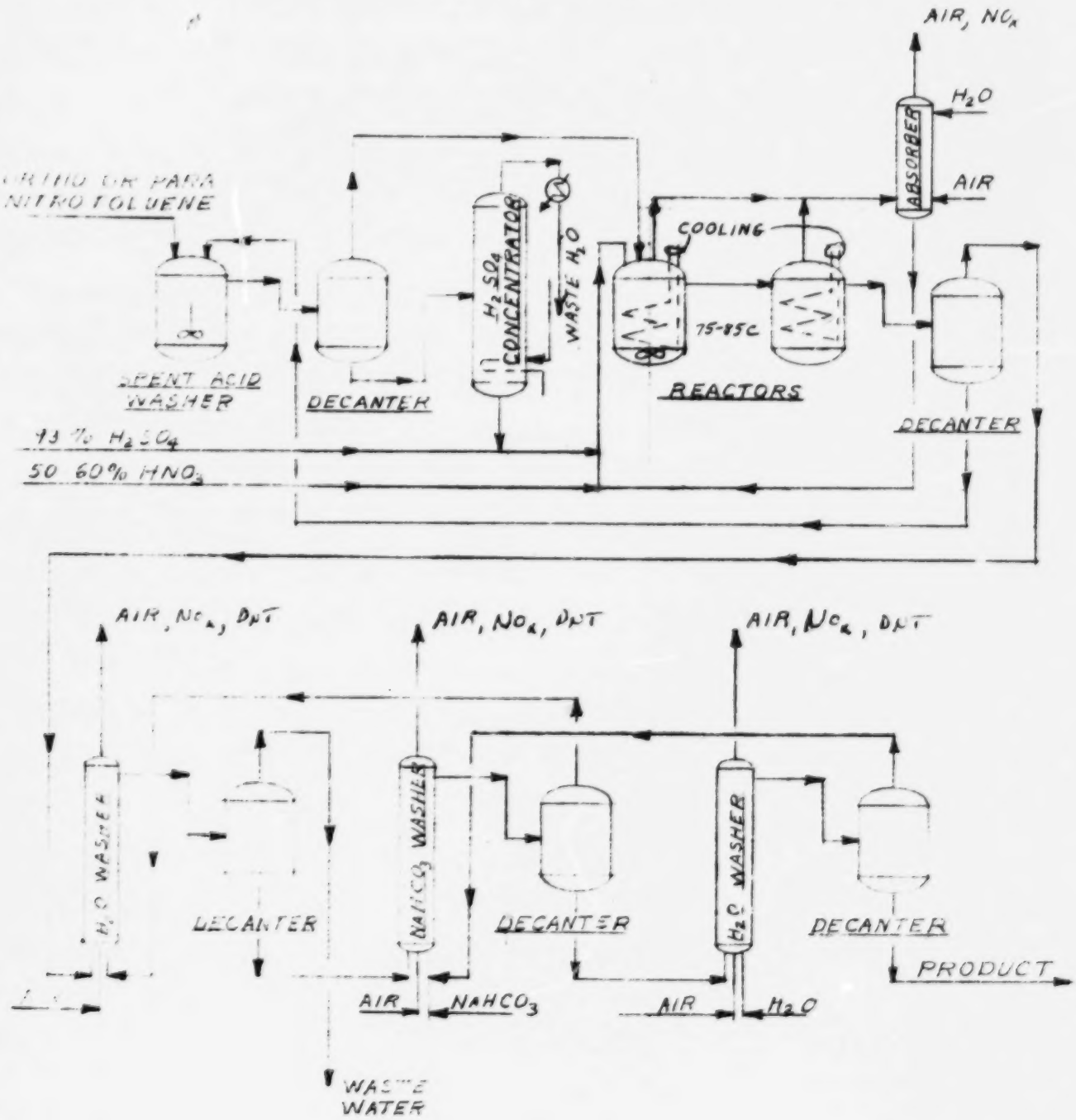
Location

Checked by Date

Subject NITRATION STUDY

Computed by GNT Date 10-28-71

PROCESS: DIRECT NITRATION OF O-OR P-NITROTOLUENE



O = a

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2815	CYCLIC INTERMEDIATES	DINITROTOLUENE

DATE:	PROCESS
11-15-11	NITRATION OF NITROTOLUENE

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	1	5
PRODUCT : COLS. 5-8	X		1	3	6
PROCESS : COLS. 9-13				5	4

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
33	ALLIED	MOUNDSVILLE, WV	B	30	B
15	DUPONT	DEEPWATER, NJ	B	170	B
11	MOBAY	NEW MARTINSVILLE WV	B	70	B
223	UNION CARBIDE	INSTITUTE, WV	A	50	A
53	PUBLICON	GEISMAR, LA	B	100	C
13	NOPCO	LINDEN, NJ	B	10	B

COMPUTER CODE NOS.

AQCR 19–22	STATE 23 24	CITY 25–36	COMPANY 37–48	49	50	51	CAPACITY 52–55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

1 of 2

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2815	CYCLIC (INTERMEDIATES	DINITROTOLUENE	SIC. NO. : COLS. 1-4 — X 2 8 1 5
DATE PREPARED	PROCESS NITRATION OF NITROTOLUENE	SOURCE ABSORBER	PRODUCT : COLS. 5-8 — X 1 3 6
1-15-71			PROCESS : COLS. 9-13 — 5 4
			SOURCE : COLS. 14-17 — X 1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	3.36	C
$C_7H_7NO_2$	NIL	A
$C_7H_6(NO_2)_2$	NIL	A

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				
"				
"				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	24 UNCON EMISS 30	Q 31	32 CEF 35	Q 36	37 SCF 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

2 of 2

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2815	CYCLIC INTERMEDIATES	DINITROTOLUENE	SIC. NO. : COLS. 1-4 — X 2 8 1 5
DATE PREPARED	PROCESS NITRATION OF NITROTOLUENE	SOURCE WASHERS	PRODUCT : COLS. 5-8 — X 1 3 6
11-15-71			PROCESS : COLS. 9-13 — 5 4
			SOURCE : COLS. 14-17 — X 4 4

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	0.21	C
$C_6H_4CH_3NO_2$	NIL	A
$C_6H_3CH_3(NO_2)_2$	NIL	A

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				
"				
"				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Nitrochlorobenzene

Nitrochlorobenzene is produced by nitrating chlorobenzene,

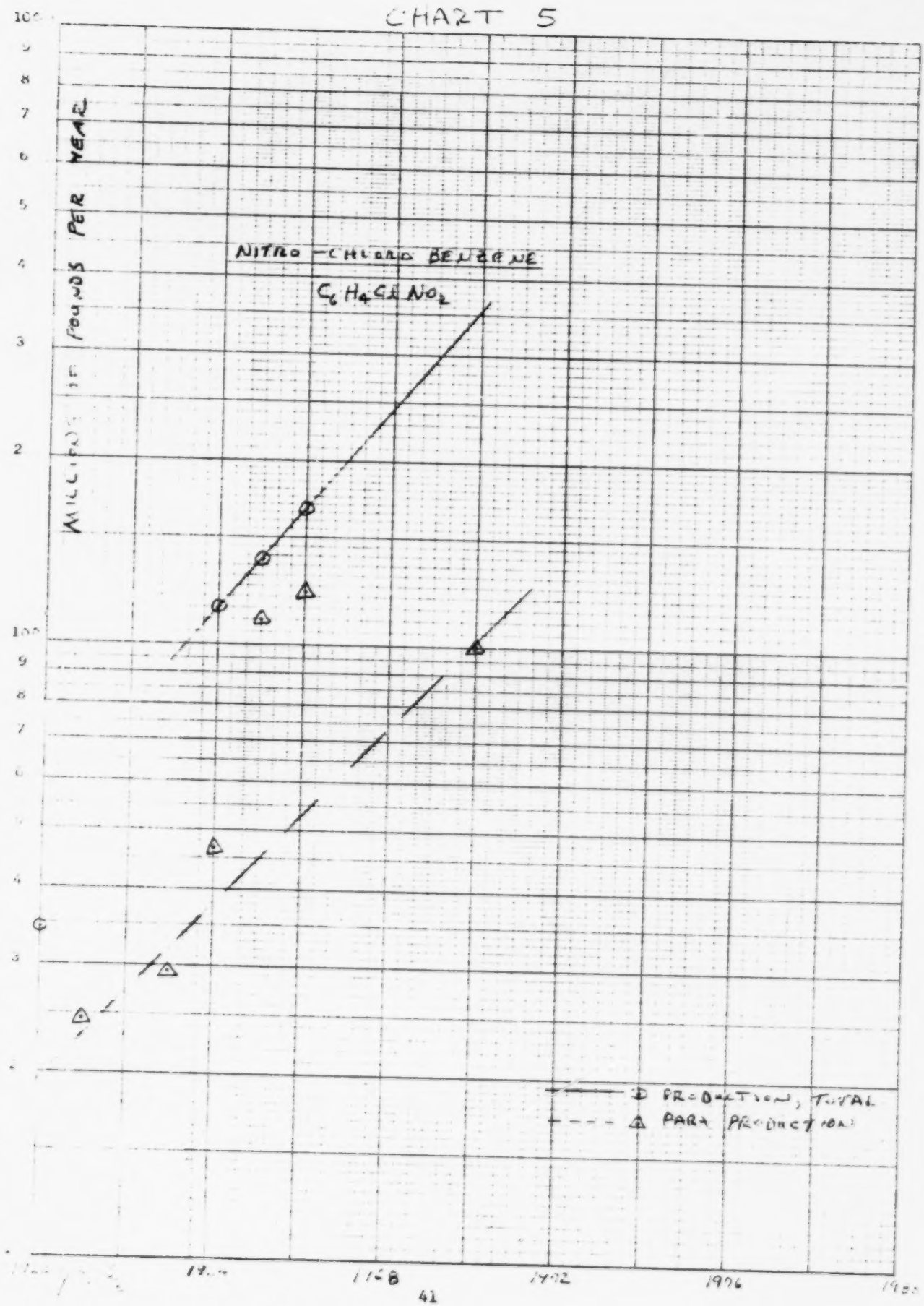
$$C_6H_5Cl + HONO_2 \longrightarrow C_6H_4ClNO_2 + H_2O$$

The chloro group increases the reactivity of benzene, making the reaction easy to carry out.

The alternate route to nitrochlorobenzene, namely, nitration of benzene followed by chlorination, does not proceed smoothly, and has lower yields and more side reactions. There is no industrial process based on these reactions.

Chart 5 shows a plot of the production data of all nitrochlorobenzenes. About 80 percent of this production is for paranitrochlorobenzene, a plot of which is also shown. Due to fluctuations in the pesticide market, no sustained growth in nitrochlorobenzene production is expected. Nitrochlorobenzene is used as an intermediate.

CHART 5


MILLIONS OF POUNDS PER YEAR
NITRO-CHLORO BENZENE
$C_6H_4ClNO_2$
PRODUCTION, TOTAL
PARA PRODUCTION
1968
1972
1976

Process: Nitration of Chlorobenzene

a. Feed Preparation

Mixed acid containing 53 percent H_2SO_4, 35 percent HNO_3 and 12 percent H_2O is prepared by mixing 50 to 60 percent HNO_3 with 93 percent H_2SO_4 and 97 percent HNO_3. The latter two acids are produced in the acid concentration system.

b. Reaction Conditions

The reaction is usually a batch process. A typical process uses a 2,640 gallon reactor equipped with an agitator and with a jacket and internal coils for cooling. The reactor is charged with 5,500 pounds of spent acid and 10,000 pounds of monochlorobenzene. The agitator is started, and 15,600 pounds of mixed acid is fed over a period of 9 hours. The temperature is permitted to rise from 20C to 50C during the 9 hours. When the reaction is complete, the batch is allowed to settle for 3 hours. The spent acid layer is drawn off to the spent acid washer and the crude chloronitrobenzene is transferred to the crude washer.

The spent acid is washed with a fresh charge of monochlorobenzene, to be used in a subsequent nitration batch to remove nitrobodies from the acid. The acid is then sent to acid concentration.

The overall process yield is not available.

c. Product Purification

The crude chloronitrobenzene is washed three times with water, followed by washing with dilute caustic and water. The charge is then dried at 90 to 100C under vacuum.

The crude chloronitrobenzene contains about 65 percent of the para isomer, about 34 percent of the ortho isomer and 1 percent of the meta isomer. These are separated and purified by alternate crystallization and distillation steps.

The crude is first cooled to 16C in a crystallizer. About 50 percent of the para isomer crystallizes out as a pure component and is separated from the mother liquor. The mother liquor is then distilled under vacuum. The first cut is primarily unreacted monochlorobenzene, with traces of meta chloronitrobenzene. This is redistilled to recover the chlorobenzene for recycle and a meta crude product containing 60 percent meta chloronitrobenzene. The second cut is predominantly the para isomer. This is crystallized out to obtain the para isomer as a product, while the mother liquor is recycled to the mother liquor tank. The third distillation cut is a slop cut and is returned to the mother liquor tank. The still residues are distilled without the column. The overheads go to a crystallizer, where the ortho isomer product crystallizes out. The mother liquor from this crystallization is returned to the mother liquor tank. The residues from the final distillation are a waste material. Product purities are not available.

d. Recycle Systems

There are several recycle streams which result during the product purification steps. These were discussed under product purification.

Another recycle stream is the spent acid stream from the reaction. This acid is fed to the denitrating column. In this column, the oxides of

nitrogen and any HNO_3 are driven overhead as a gas while the water is held back by the sulfuric acid. The sulfuric acid leaves the bottom of the column at about 60 to 70 percent H_2SO_4 and is fed to a sulfuric acid concentrator where the water is driven off and a 92 to 93 percent sulfuric acid is produced for feed to the mixed acid tank. The overheads from the denitrating tower go to a bleacher, where they contact air and the NO is oxidized. The gases then pass through a reflux condenser where 97 percent HNO_3 is condensed and returns to the bleacher and is transferred to the mixed acid tank. The gases from the reflux condenser go to the absorber where the oxides of nitrogen are absorbed in water and some fresh nitric acid. The bottoms from this absorber are recycled to the denitration tower.

e. Raw Materials

This process uses two raw materials, monochlorobenzene and 50 to 60 percent nitric acid. Some makeup sulfuric acid is required.

f. By-products

This process produces ortho chloronitrobenzene, para chloronitrobenzene, and a crude containing 60 percent meta chloronitrobenzene.

g. Sources of Air Pollution

There are two usual sources of air pollution. The first is the vent from the reactor, which contains oxides of nitrogen. The second vent is from the absorber in the acid concentration system, which contains air and unabsorbed oxides of nitrogen. If the plant has a drum type sulfuric acid concentrator, instead of a distillation type concentrator, a vent exists which will contain flue gases and entrained sulfuric acid vapor and organics vapor.

Pk 109

FLOW DIAGRAM
CHLORO NITROBENZENE MANUFACTURE

Job EPA

Location

Subject NITRATION STUDY

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

File No 3382 Sheet No

Checked by Date

Computed by GNT Date 10-22-71

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2815	CYCLIC INTERMEDIATES	NITROCHLORO-BENZENE

DATE:	PROCESS
11-12-71	NITRATION OF CHLORO BENZENE

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	1	5
PRODUCT : COLS. 5-8	X		1	3	4
PROCESS : COLS. 9-13				5	2

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
104	AMER. ANILINE	LOCKHAVEN, PA	A	10	A
15	DU PONT	DEEPWATER, NJ	A	30	A
264	MONSANTO	SAUGET, IL	B	85	A

COMPUTER CODE NOS.

AQCR 19–22	STATE 23 24	CITY 25–36	COMPANY 37–49	X 50	51	CAPACITY 52–55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2815	CYCLIC INTERMEDIATES	NITROCHLORO-BENZENE	SIC. NO. : COLS. 1-4 — X 2 8 1 5
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8 — X 1 3 4
11-15-71	NITRATION OF CHLORO-BENZENE	REACTOR	PROCESS : COLS. 9-13 — 5 2
			SOURCE : COLS. 14-17 — X 3 [illegible]

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	NIL	B
C_6H_5Cl	3.2	C
$C_{11}H_6ClNO_2$	NIL	A

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				
"				
"				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2815	CYCLIC INTERMEDIATES	NITROCHLORO-BENZENE	SIC. NO. : COLS. 1-4 — X 2 8 1 5
DATE PREPARED 11-15-71	PROCESS NITRATION OF CHLORO-BENZENE	SOURCE ARSORBER	PRODUCT : COLS. 5-8 — X 1 3 4
			PROCESS : COLS. 9-13 — 5 2
			SOURCE : COLS. 14-17 — X 1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NOx	0.9	C

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO 18–20	CNO 21–23	UNCON EMISS 24–30	Q 31	CEF 32–35	Q 36	SCF 37–40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

2. Industrial Organic Chemicals, Not Elsewhere Classified - SIC Industry No. 2818

Establishments primarily engaged in manufacturing industrial organic chemicals not elsewhere classified. Important products include:

Non-cyclic organic chemicals
Solvents
Polyhydric alcohols
Synthetic perfume and flavoring materials
Rubber processing chemicals
Plasticizers
Synthetic tanning agents
Chemical warfare gases
Esters, amines, etc., of polyhydric alcohols

Some of the nitro compounds are:

Acrylonitrile
Adipic acid
Adiponitrile
Ethyl nitrite
Malononitrile
Oxalic acid

For this study, these products have been studied:

Nitroparaffins
Adipic acid
Oxalic acid
Acrylonitrile

The production of these four products consume about 11 percent of the nitric acid production.

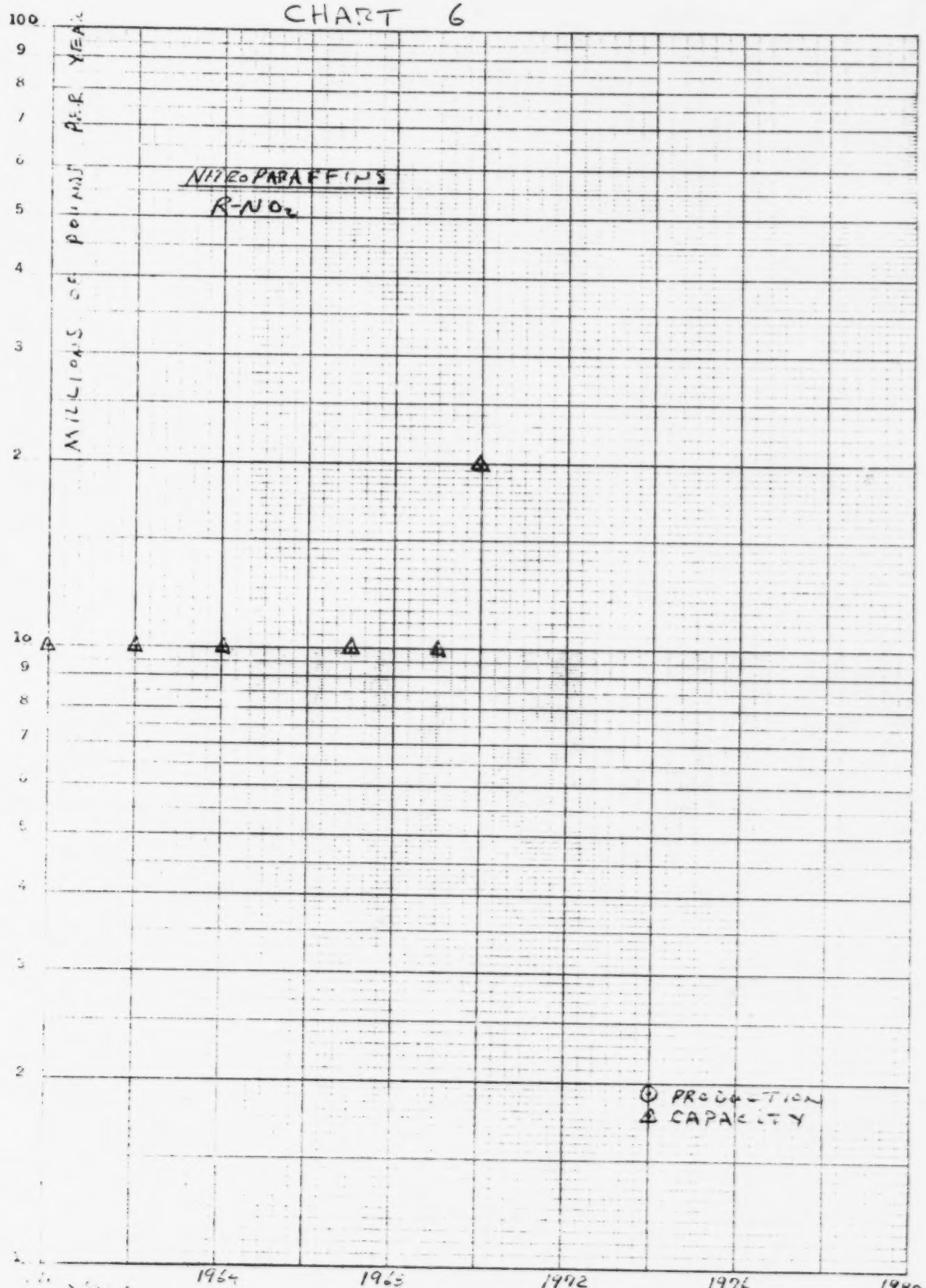
Product: Nitroparaffins

Nitroparaffins are made by nitrating light aliphatics in the vapor phase,

$$C_3H_8 + HONO_3 \longrightarrow C_3H_7NO_2 + H_2O$$

Commercial Solvents has pioneered this family of compounds, having their main production plant in Louisiana with a semi-works in Peoria. The nitroparaffins are used as intermediates and solvents. The annual growth rate is estimated at less than 5 percent. There is no published production data. Chart 6 shows the capacity data.

CHART 6


MILLIONS OF POUNDS PER YEAR
100
9
8
7
6
5
4
3
2
10
9
8
7
6
5
4
3
2
NITROPARAFFINS
R-NO2
PRODUCTION
CAPACITY
1964
1968
1972
1976
1980

Process: Nitration of Paraffins

a. Feed Preparation

There is no feed preparation.

b. Reaction Conditions

The reaction is carried out continuously. Propane is vaporized and heated to 370 to 450C, and is fed to the reactor at 125 to 175 psig. In the reactor, 50 to 60 percent nitric acid is sprayed into the propane gas. About five moles of propane per mole of HNO_3 are fed. The heat of reaction vaporizes the nitric acid. The reactor operates adiabatically.

The desired reaction products are nitromethane, nitroethane, 1-nitropropane and 2-nitropropane. A typical distribution is 10 percent nitromethane, 25 percent nitroethane, 25 percent 1-nitropropane, and 40 percent 2-nitropropane. By varying the reaction conditions, the relative amounts of nitroparaffin may be controlled. Normal ranges, with propane as a raw material, are nitromethane 10 to 30 percent, nitroethane 20 to 25 percent, nitropropanes 55 to 65 percent.

The purities of the finished nitroparaffin products are all 99 percent plus nitroparaffins. The minimum purity of the individual products is nitromethane 95 percent, nitroethane 90 percent, 1-nitropropane 94 percent, and 2-nitropropane 94 percent.

With recycling, the nitroparaffin yield, based on nitric acid, approaches the theoretical yield. Some 90 plus moles of nitroparaffins are produced per 100 moles of HNO_3 used up. No information is available on yields based on propane fed.

c. Product Purification

The product gases from the reactor pass through a cooler and condenser in series. The nitroparaffins condense and the mixture is brought down to atmospheric pressure. The remaining vapor contains nitric oxides, some inerts, unreacted propane, and a small quantity of aldehydes, ketones, etc.

The cooled mixture is fed to an absorber where all components except nitric oxides, inerts, and unreacted propane are absorbed in a solvent such as hydroxylamine hydrochloride. The off gases go to a recovery process which is discussed under recycle systems. The main reason for the absorption step is to insure that the aldehydes, ketones, etc., are not recycled with the propane. The bottoms from the absorption column go to the stripper where steam is used to strip the reaction products from the solvent. The solvent is removed from the bottom of the stripper and is recycled to the absorber. The overheads from the stripper are condensed and fed to a decanter. The bottom layer, which is water, is returned to the stripper. The light layer is fed to the heads column, where aldehydes, ketones and other light boilers are separated as overheads and become a by-product.

The bottoms from the heads column are treated with chemicals (unidentified) and then washed with water to remove chemical products that would cause corrosion in the subsequent purification steps.

The reaction products, after the washing step, consist of nitroparaffins and higher boiling compounds saturated with water. This mixture is fed to a drying column where the water is removed overhead and returned to the decanter following the washing step. The bottoms from the drying column are fed

to four distillation columns in series, where the nitroparaffins are separated into four products, nitromethane, nitroethane, 2-nitropropane, and 1-nitropropane. The bottoms from the last column are high boilers (heavies) and are a waste product.

d. Recycle Systems

The off gases from the absorber consisting of nitric oxides, unreacted propane, and CO_2 are fed to a separation system. Details of this system are not available. However, it is assumed that it consists of an adsorption step which separates the unreacted propane from the nitric oxides and CO_2. The propane is recycled to the reactor. The nitric oxides and CO_2 pass through an oxidizer where NO is oxidized. This is followed by an absorber where the oxides of nitrogen are absorbed in water to produce nitric acid. The nitric acid is recycled to the reactor. The off gases, consisting of air, N_2, CO_2, and unabsorbed oxides of nitrogen, are vented.

e. Raw Materials

Two major raw materials are used. These are propane and 50 to 60 percent nitric acid. Minor raw materials are the unidentified chemicals used in the chemical treatment step, and hydroxylamine hydrochloride required for makeup for losses in the absorption and stripping steps.

f. By-products

This process produces one by-product, the overheads from the heads column, containing aldehydes and ketones. This is either a waste product or undergoes further processing to produce salable products.

R. Sources of Air Pollution

The only pollution source is the vent from the nitric acid absorber. This vent will contain air, CO_2 and unabsorbed oxides of nitrogen.

PR 109

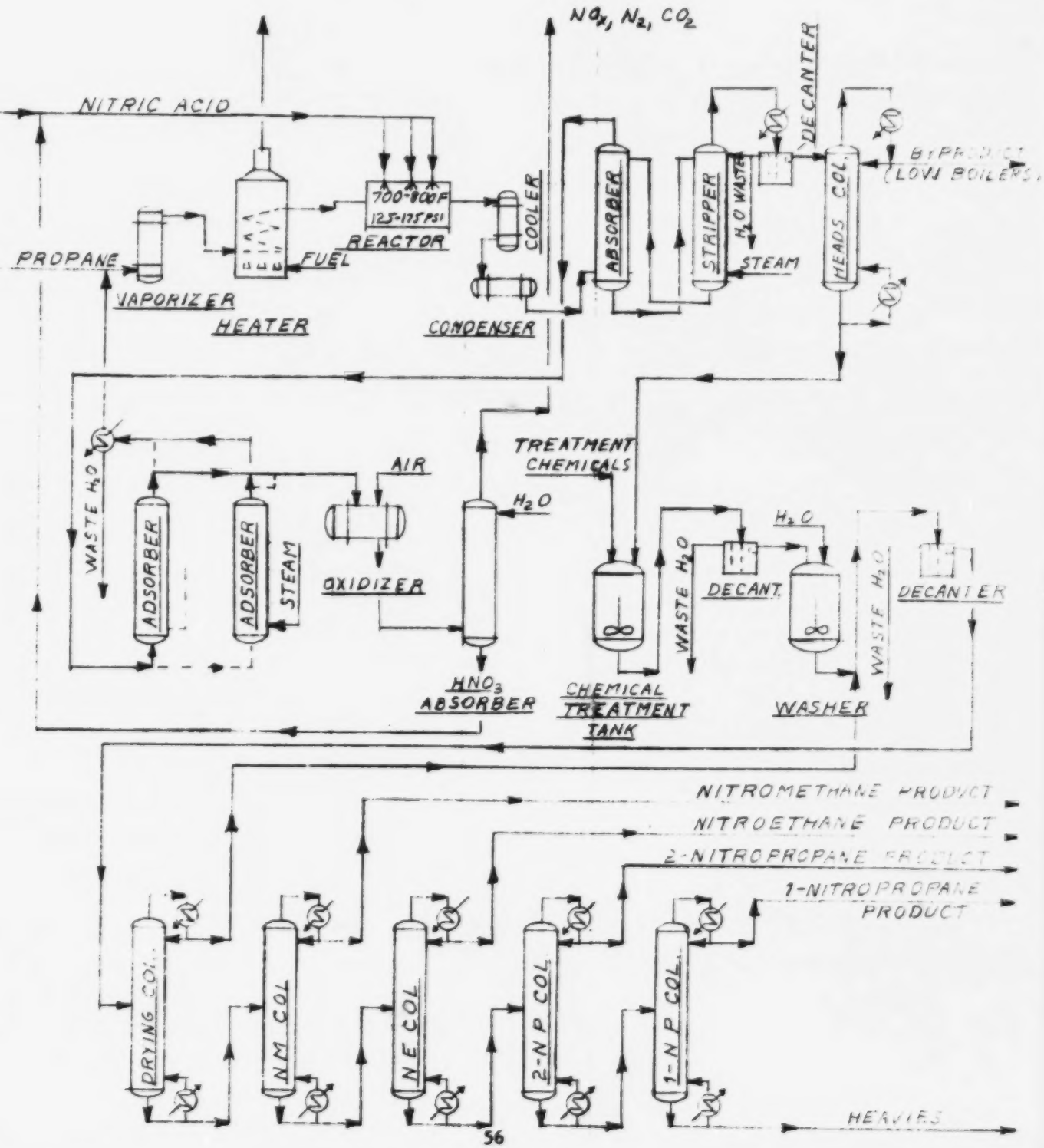
FLOW DIAGRAM
NITROPARAFFINS MANUFACTURE

Job EPA — PROCESSES RESEARCH, INC. — File No 3382 — Sheet No

Location — INDUSTRIAL PLANNING AND RESEARCH — Checked by — Date

Subject NITRATION STUDY — CINCINNATI NEW YORK — Computed by G.N.T. — Date 11-1-71

PROCESS: NITRATION OF PROPANE (TYPICAL)



PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2818	IOC	NITRO PARAFFINS

DATE:	PROCESS
11-16-71	NITRATION OF LIGHT ALIPHATICS (PARAFFINS)

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	1	8
PRODUCT : COLS. 5-8	X		1	4	0
PROCESS : COLS. 9-13				5	8

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
UNCL	COMMERCIAL SOLVENTS	STERLINGTON, LA	A	21	A

COMPUTER CODE NOS.

AQCR 19–22	STATE 23 24	CITY 25–36	COMPANY 37–49	X 50	CAPACITY 51 52–55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2818	IOC	NITRO PARAFFINS	SIC. NO. : COLS. 1-4 — X 2818
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8 — X 140
11 16 71	NITRATION OF LIGHT (PARAFFIN) ALIPHATICS	ABSORBER (HNO_3)	PROCESS : COLS. 9-13 — 58
			SOURCE : COLS. 14-17 — X 1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO,	1.5	C

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Adipic Acid

Adipic acid is made by oxidizing crude cyclohexanol. The oxidizing agent can be nitric acid,

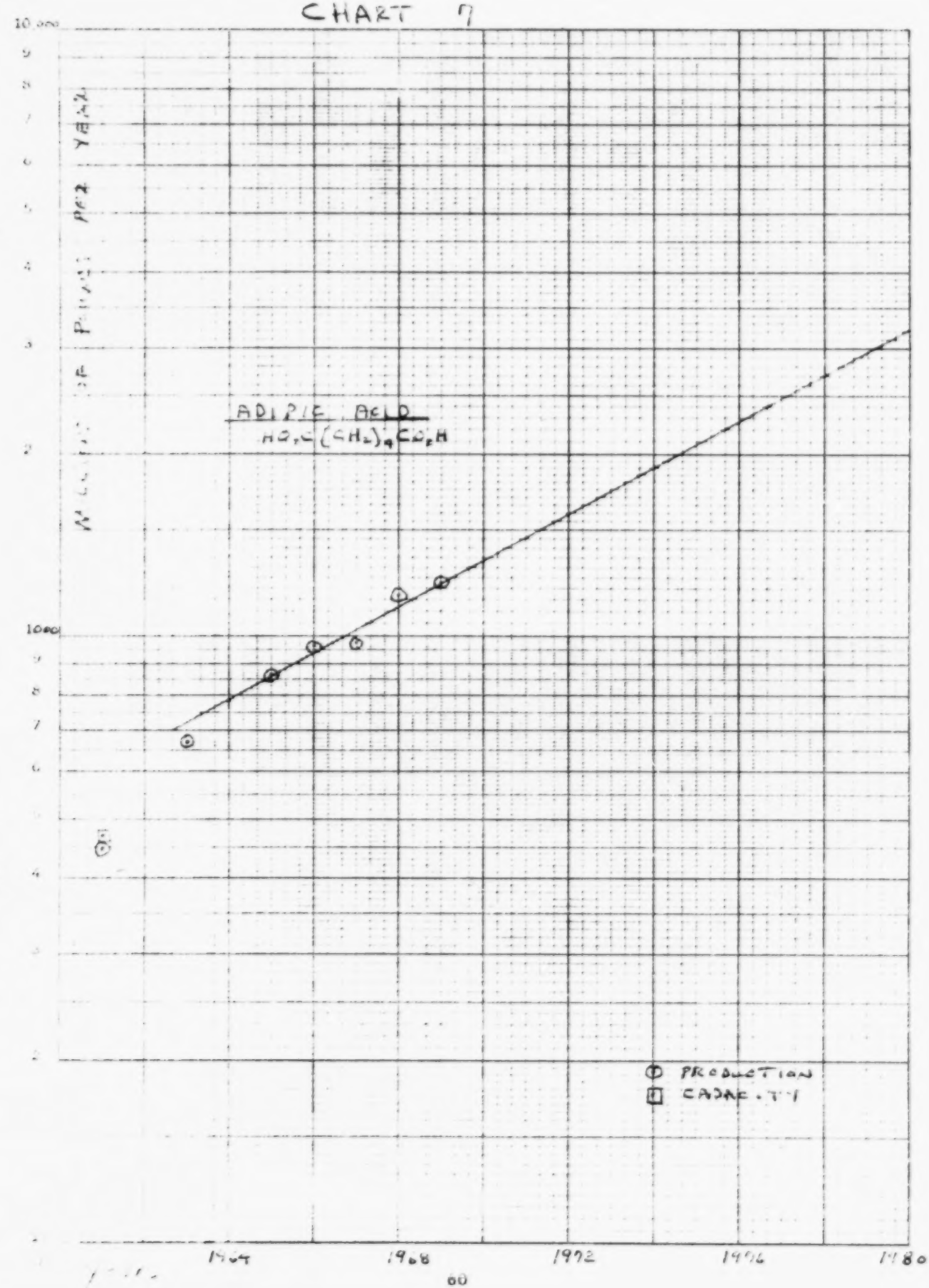
$$C_6H_{11}OH + 2HNO_3 \longrightarrow (COOH)_2(CH_2)_4 + N_2O + 2H_2O$$

by which over 90 percent of the adipic acid is made. Or it can be air,

$$C_6H_{11}OH + 2\ 1/2\ O_2 \qquad (COOH)_2(CH_2)_4 + 2H_2O$$

In 1970, the production of adipic acid had exceeded 1.3 billion pounds. For the Seventies, a 20 percent growth rate is expected. See Chart 10 for production data. Adipic acid is a nylon intermediate.

CHART 7


10,000
1000
ADIPIC ACID
HO₂C(CH₂)₄CO₂H
1964
1968
1972
1976
1980
PRODUCTION
CAPAC. T.Y.

Process: Oxidation of Cyclohexanol to Adipic Acid

a. Feed Preparation

The cyclohexanol feed is a crude mixture of cyclohexanol and cyclohexanone. This crude is usually obtained by the air oxidation of cyclohexane at 125 to 160C and 50 to 250 psi in the presence of cobalt naphthenate catalyst. The reactor product is distilled to remove water and unreacted cyclohexane. Another method for obtaining the cyclohexanol crude is from the hydrogenation of phenol at 300F and 50 psig in the presence of a palladium catalyst. The cyclohexanol crude leaves the reactor as a vapor with unreacted hydrogen. The cyclohexanol crude is separated from the hydrogen to become the desired feed material for adipic acid production.

b. Reaction Conditions

Cyclohexanol crude is oxidized to adipic acid using 40 to 50 percent nitric acid. The nitric acid fed is at least 1.5 times stoichiometric. The reaction is carried out at 50 to 150C and 50 to 250 psig in the presence of a catalyst consisting of ammonium metavanadate and copper. Based on cyclohexane content of feed, a yield of 60 to 70 percent adipic acid is obtained.

c. Product Purification

The reactor liquid product is air stripped to remove nitrous oxide. It is then steam distilled to remove unreacted nitric acid and low boiling organics (as overheads).

The liquid from the bottoms of the steam still are cooled to 40 to 50C. This crystallizes out the adipic acid. The crystals are separated from the mother liquor, redissolved in water, and recrystallized to remove impurities. The crystals are dried to produce the adipic acid.

d. Recycle Systems

The reaction produces nitrous oxide as a gas. This is oxidized with air, and scrubbed with water to produce nitric acid, which is recycled to the reactor.

The overheads from the steam still contain nitric acid which is recovered and recycled to the reactor.

A portion of the mother liquor from the first crystallization step, which contains nitric acid and catalyst, is recycled to the reactor. Another portion is fed to a still. The overheads from the still, containing water and nitric acid, are recycled to the reactor. The bottoms are cooled to crystallize out adipic acid, which is combined with the crystals from the first crystallization step. The mother liquor is distilled to recover any nitric acid present. This is concentrated and recovered. The bottoms is either a waste material or undergoes additional processing to recover the catalyst.

e. Raw Materials

The raw materials consist of the crude cyclohexanol (which is discussed under feed preparation), 50 percent nitric acid which is obtained by recycle from the process, and the catalyst which is ammonium vanadate and copper turnings.

f. By-products

The process yields no salable by-products.

g. Sources of Air Pollutants.

There are two sources of air pollutants. The first is the effluent from the oxidizer. This effluent will be air with any residual unoxidized and unabsorbed nitrous oxide or nitrogen dioxide. The other source is the vent from product drying which will contain product particulates as a contaminate.

PR 109

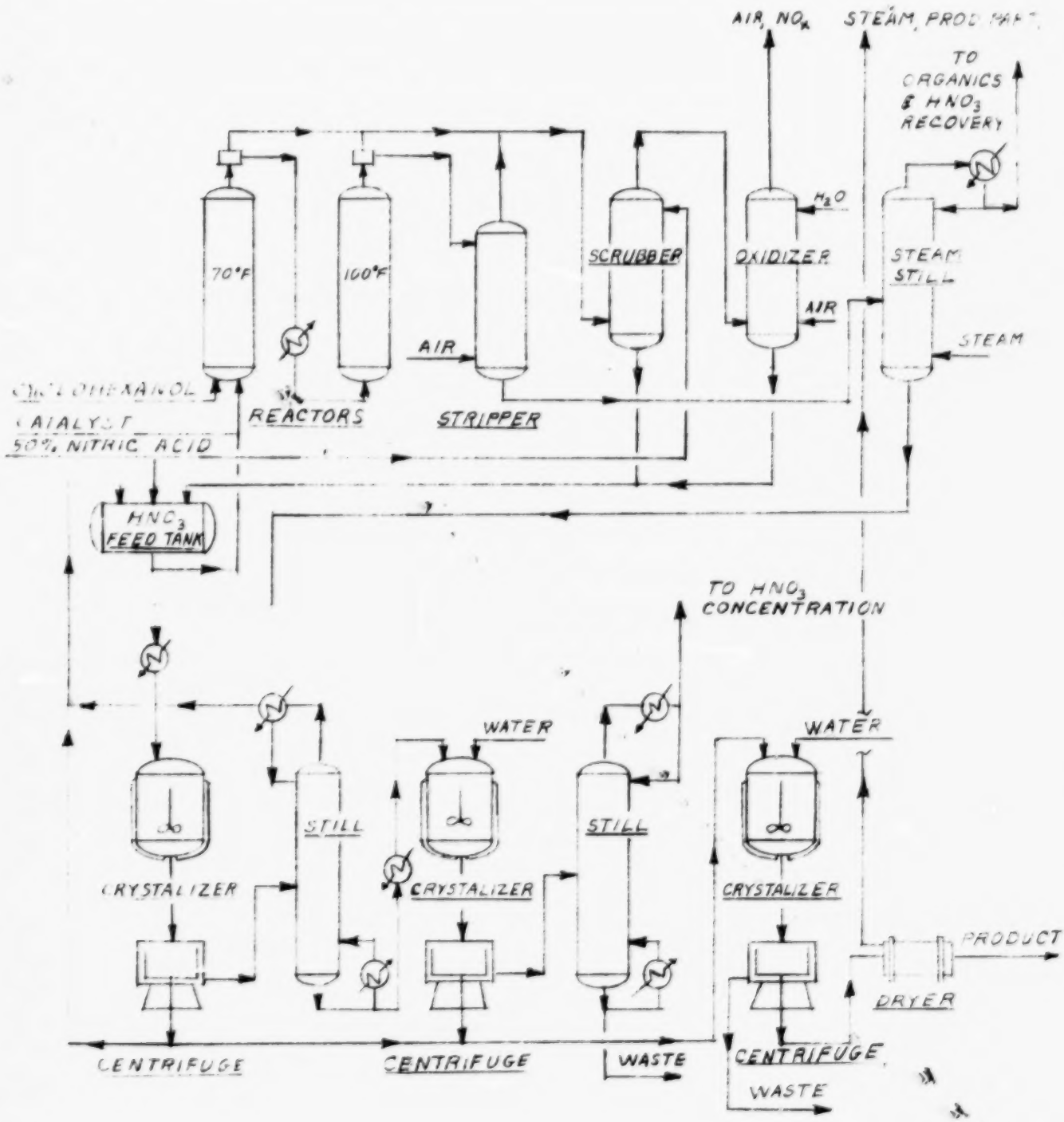
FLOW DIAGRAM
ADIPIC ACID MANUFACTURE

Job EPA — PROCESSES RESEARCH, INC. — File No 3382 Sheet No ____

Location ____ — INDUSTRIAL PLANNING AND RESEARCH — Checked by SPK Date 10-[illegible]

Subject NITRATION STUDY — CINCINNATI NEW YORK — Computed by GNT Date 10-20-71

PROCESS: NITRIC ACID OXIDATION OF CRUDE CYCLOHEXANOL



PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2818	IOC	ADIPIC ACID

DATE:	PROCESS
11-16-81	OXIDATION OF CYCLOHEXANOL

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	1	8
PRODUCT : COLS. 5-8	X		1	4	1
PROCESS : COLS. 9-13				5	9

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
145	ALLIED	HOPEWELL, VA	A	20	B
55	CELANESE	BAY CITY, TX	A	35	B
65	MONSANTO	PENSACOLA, FL	A	320	B
53	MONSANTO	LULING, LA	B	30	B
170	DUPONT	BELLE, WV	A	210	B
55	DUPONT	ORANGE, TX	A	210	B
155	EL PASO	ODESSA, TX	A	40	B

COMPUTER CODE NOS.

AQCR 19–22	STATE 23 24	CITY 25–38	COMPANY 37–49	X 50 51	CAPACITY 52–55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT
2818	IOC	ADIPIC ACID
DATE PREPARED	PROCESS	SOURCE
11-16-'11	OXIDATION OF CYCLOHEXANOL	ABSORBER (OXIDIZER)

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	1	8
PRODUCT : COLS. 5-8	X		1	4	1
PROCESS : COLS. 9-13				5	9
SOURCE : COLS. 14-17	X				1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	12	A

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO 18–20	CNO 21–23	UNCON EMISS 24–30	Q 31	CEF 32–35	Q 36	SCF 37–40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2818	IOC	ADIPIC ACID	SIC. NO. : COLS. 1-4 — X 2818
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8 — X 1411
11-16-71	OXIDATION OF CYCLOHEXANOL	DRYER	PROCESS : COLS. 9-13 — 5 9
			SOURCE : COLS. 14-17 — X 1 1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
Particulates	1.8	B

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO (18-20)	CNO (21-23)	UNCON EMISS (24-30)	Q (31)	CEF (32-35)	Q (36)	SCF (37-40)	Q (41)	YR (42)	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Oxalic Acid

The main source of oxalic acid is as a by-product from citric acid production, using fermentation,

$$\text{(Sugars)} \xrightarrow{\text{Mold}} (COOH)_2 + \text{(By-products)}$$

Oxalic acid is also made from formates,

$$NaOH + CO \longrightarrow HCOONa$$

$$2HCOONa \longrightarrow (COONa)_2 + H_2$$

$$(COONa)_2 + Ca(OH)_2 \longrightarrow Ca(COO)_2 + 2\ NaOH$$

$$Ca(COO)_2 + H_2SO_4 \longrightarrow (COOH)_2 + CaSO_4$$

It is estimated that about 10 percent of the oxalic acid production is made by a third process, the nitric acid oxidation of glucose,

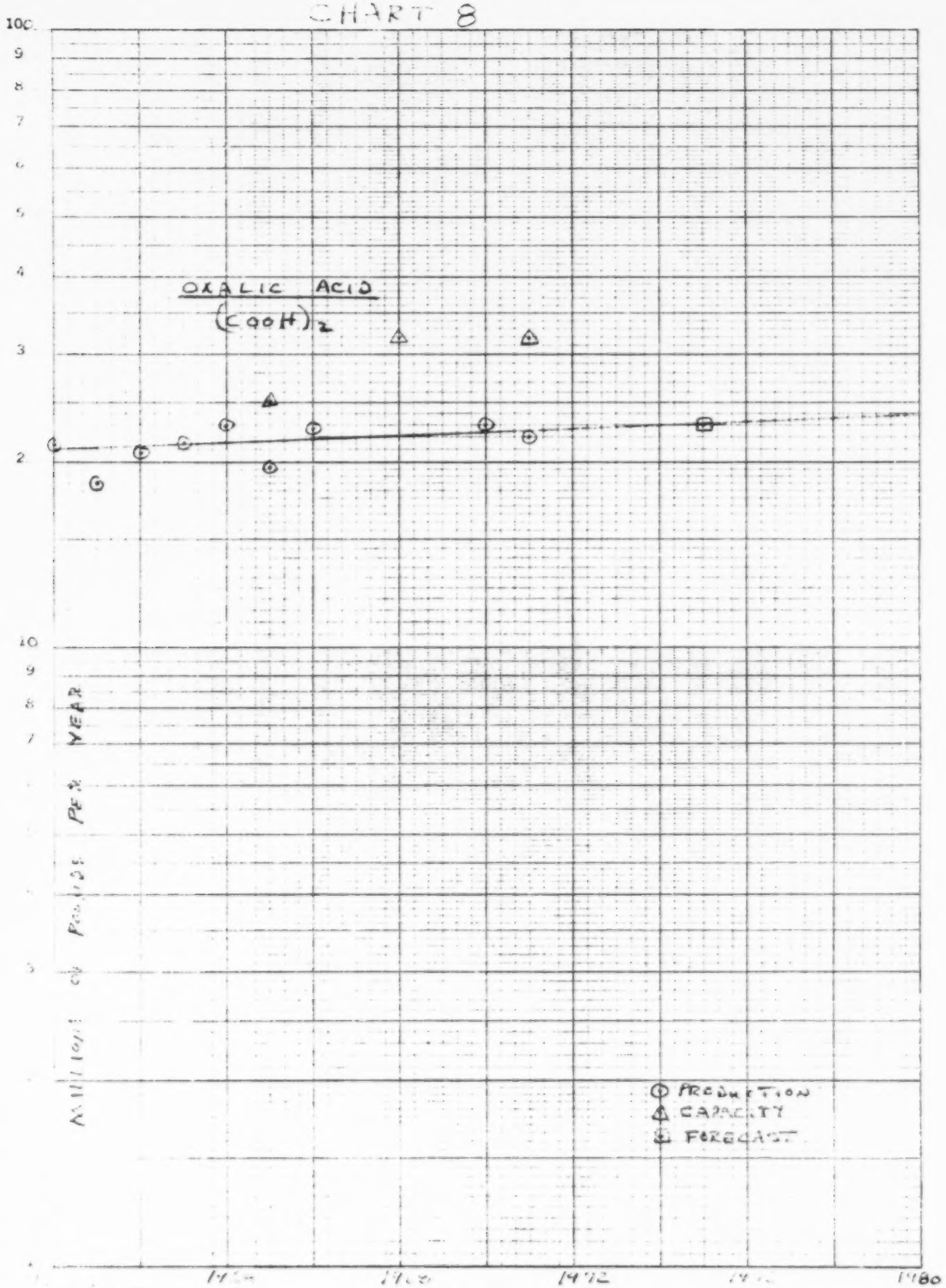
$$C_6H_{12}O_6 + 6HNO_3 \longrightarrow 3(COOH)_2 + 6H_2O + 6NO$$

with 70 percent yields and a high purity product.

In 1970, about 23 million pounds of oxalic acid was produced. Its main uses are textile finishing, metal cleaning, and as an intermediate. Chart 8 shows a plot of the production data. For the Seventies, little growth in oxalic acid production is expected.

In the late Sixties, there was a shift in oxalic acid producers. Hooker, Stauffer, Miles, and Victor abandoned this business, while Pfizer and Allied expanded.

CHART 8


OXALIC ACID
(COOH)2
MILLIONS OF POUNDS PER YEAR
PRODUCTION
CAPACITY
FORECAST
1980

Process: Oxidation of Glucose to Oxalic Acid

a. Feed Preparation

Glucose is obtained from raw starch. The raw starch (85 percent) is dispersed by slurrying it in approximately an equal amount of 11 percent oxalic acid solution at 75 to 80C. After refluxing for approximately 6 hours, virtually all the starch is hydrolyzed to a monosaccharide, chiefly glucose.

b. Reaction Conditions

The process is usually run as a batch process. The hydrolyzed starch solution, containing about 60 percent glucose (monosaccharide), is mixed with oxalic acid mother liquor recovered from the filtration step of a previous run. This mother liquor is fortified with sulfuric acid and catalyst to compensate for process losses. The adjusted mother liquor contains approximately 50 percent sulfuric acid, 5 percent oxalic acid, 0.5 percent ferric iron (as ferric sulfate), and 0.005 percent vanadium (as vanadium pentoxide). The glucose mother liquor solution is heated to about 70C with agitation. Nitric acid of 65 to 95 percent strength is gradually added at a rate as necessary to maintain the temperature at 70C. External cooling is generally used. One part of 60 percent glucose solution is used with 2.5 parts of 90 percent nitric acid and 7.5 parts of 50 percent sulfuric acid liquor. Oxides of nitrogen evolved during the reaction go to the absorption concentration system (discussed under recycle systems).

The solution from the reactor is cooled in a crystallizer to 24 to 35C. The resulting slurry is filtered. The mother liquor is returned to a subsequent reactor run.

The filter cake from the filter can be dried to give an oxalic acid dihydrate of 90 percent purity, or it can be dissolved in an equal weight of water at 65C and recrystallized at 24C. In the latter case, the slurry is filtered, the mother liquor is returned to the dissolver, and the filter cake is dried at less than 65C to yield an oxalic acid dihydrate product which assays 97 to 99 percent.

c. Recycle Systems

The nitric oxides from the reactor are passed to an absorber where they are oxidized with air and absorbed in dilute nitric acid. The off gases are vented.

The nitric acid from the absorber is fed to a nitric acid dehydrator which uses sulfuric acid to dehydrate the nitric acid. The 90 percent nitric acid produced is recycled to the reaction step, while the dilute sulfuric acid formed goes to a sulfuric acid concentrator to be concentrated to 93 percent sulfuric acid, for recycle to the nitric acid dehydrator.

d. Raw Materials

The major raw material is starch, which is hydrolized to glucose. Other raw materials are makeup 93 percent sulfuric acid, makeup 90 percent nitric acid, and makeup catalyst, i.e., ferric sulfate and vanadium pentoxide.

e. By-products

There are no by-products.

f. Sources of Air Pollution

There are two sources of air pollution. The vented air from the product dryer will contain product particulates. The vent from the absorber will contain air saturated with water and also unabsorbed oxides of nitrogen.

FR 109

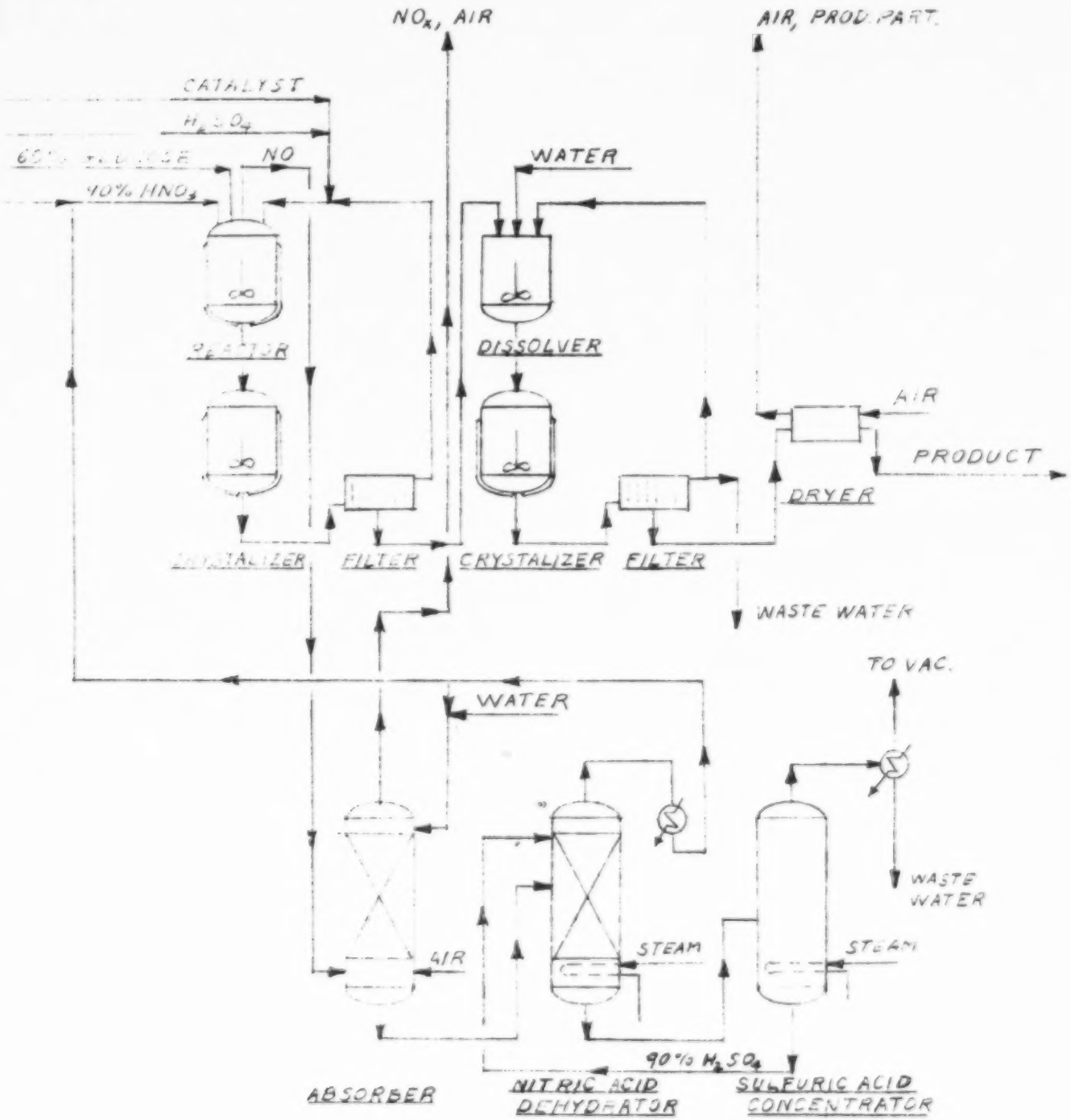
FLOW DIAGRAM
OXALIC ACID MANUFACTURE

Job EPA — PROCESSES RESEARCH, INC. — File No 3382 Sheet No ____

Location ____ — INDUSTRIAL PLANNING AND RESEARCH — Checked by ____ Date ____

Subject NITRATION STUDY — CINCINNATI NEW YORK — Computed by GNT Date 10-25-71

PROCESS: NITRIC ACID OXIDATION OF GLUCOSE



Q = C

PROCESS DATA TABULATION

SH___ OF___

SIC. NO.	INDUSTRY	PRODUCT
2818	IOC	OXALIC Acid

DATE:	PROCESS
11-18-71	OXIDATION OF GLUCOSE

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	1	8
PRODUCT : COLS. 5-8	X		1	4	3
PROCESS : COLS. 9-13				6	1

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
24	ALLIED	BUFFALO, NY	A	10	C
15	ALLIED	MARCUS HOOK, PA	A	10	C

COMPUTER CODE NOS.

AQCR 19–22	STATE 23 24	CITY 25–36	COMPANY 37–49	X 50 51	CAPACITY 52–55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2818	IOC	OXALIC ACID	SIC. NO. : COLS. 1-4 X 2 8 1 6
DATE PREPARED	PROCESS OXIDATION OF GLUCOSE	SOURCE ABSORBER	PRODUCT : COLS. 5-8 X 1 4 3
11-18-71			PROCESS : COLS. 9-13 6 1
			SOURCE : COLS. 14-17 X 1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	4.5	B

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2-1-C	IOC	OXALIC ACID	SIC. NO. : COLS. 1-4 — X 2 8 1 6
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8 — X 1 4 3
11-17-71	OXIDATION OF GLUCOSE	DRYER	PROCESS : COLS. 9-13 — 6 1
			SOURCE : COLS. 14-17 — X 1 1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
PARTICULATE	1.8	B

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO 18	CNO 20 21	UNCON EMISS 23 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Acrylonitrile

About 16 percent of the acrylonitrile is produced by this reaction, which will be studied here,

$$4C_3H_6 + 6NO \longrightarrow 4C_3H_3N + N_2 + 6H_2O$$

About half of the acrylonitrile production is made by the Sohio process, which appears to be the process of the future,

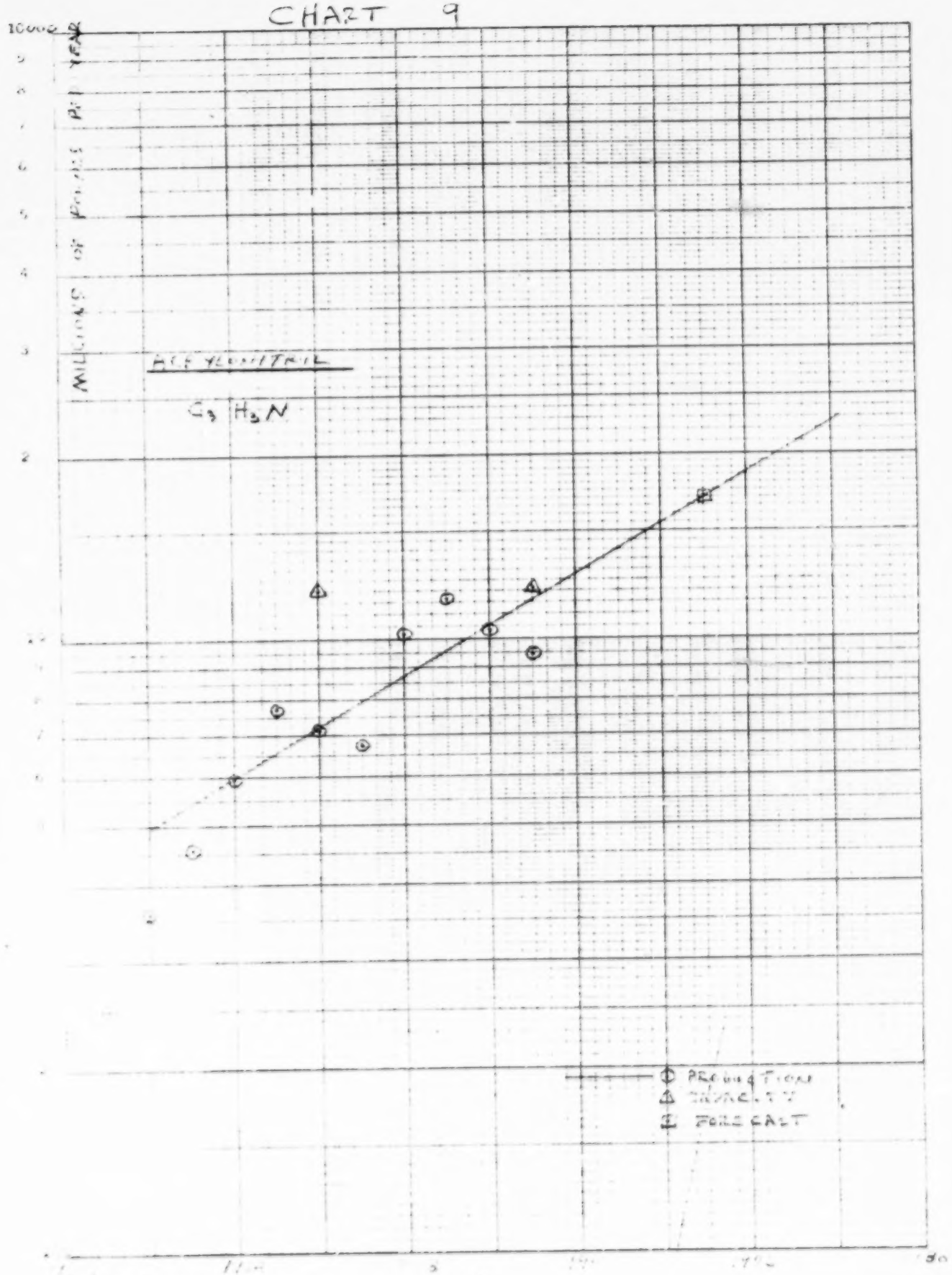
$$C_3H_6 + NH_3 + 1\text{-}1/2\ \underset{(Air)}{O_2} \longrightarrow C_3H_3N + 3H_2O$$

The remaining acrylonitrile is made from acetylene,

$$C_2H_2 + HCN \longrightarrow C_3H_3N$$

There is a fourth process, using ethylene oxide, which is obsolete. Chart 9 shows a plot of the production data. An annual growth rate of 13 percent is forecast. About 61 percent of the acrylonitrile is used for fibers. The next larger use, 17 percent, is for resins.

CHART 9


MILLIONS OF POUNDS PER YEAR
ACRYLONITRILE
C_3H_3N
PRODUCTION
INDUSTRY
FORECAST

Process: Oxidation of Propylene to Acrylonitrile

a. Feed Preparation

None

b. Reaction Conditions

Nitric oxide is reacted with proplyene in the vapor phase at 450 to 500C and atmospheric pressure. There is a large excess of propylene in the feed. The reaction mixture is diluted with air or nitrogen. The catalyst is either lead titanate or silver/silica. A product yield of 80 percent is obtained at a conversion of 12 percent.

c. Product Purification

The reaction gas product stream passes through a water scrubber where all the reaction products except nitrogen and the dilution air are absorbed. The nitrogen and air are vented. The product and by-products are recovered and purified in a train of distillation columns. Unreacted propylene is recovered and recycled to the reaction step.

d. Raw Materials

The raw materials used in the process are propylene and nitric oxide.

e. By-products

The process produces the following by-products: acetone, 1,5-hexadiene, benzene, and hydrogen cyanide.

f. Sources of Air Pollution

There is only one point where atmospheric emission occurs. This point is the vent from the scrubber. Normally, the emission will consist of nitrogen and air saturated with water vapor.

A-109

FLOW DIAGRAM
ACRYLONITRILE MANUFACTURE

Job EPA

Location

Subject NITRATION STUDY

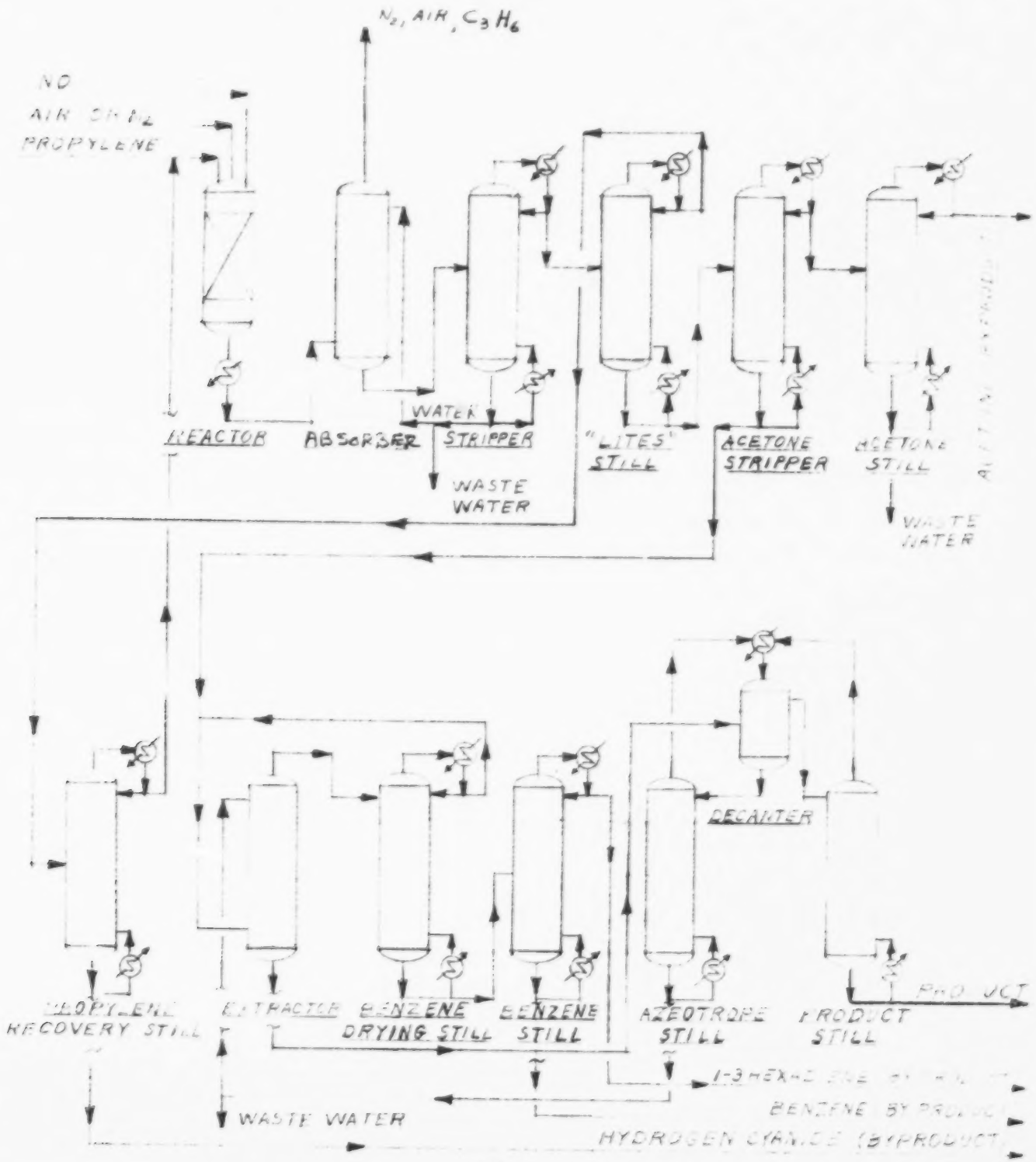
PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

File No 338 Sheet No

Checked by Date

Computed by GNT Date 10-28-68

PROCESS: NO OXIDATION OF PROPYLENE



Q = 1

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2819	IC -	ACRYLONITRILE

DATE:	PROCESS
11-17-11	NITRIC OXIDE OXIDATION OF PROPYLENE

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	1	9
PRODUCT : COLS. 5-8	X		1	4	C
PROCESS : COLS. 9-13				6	3

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
52	DUPONT	BEAUMONT TX	A	20.	A

COMPUTER CODE NOS.

AQCR 18–22	STATE 23 24	CITY 25–36	COMPANY 37–49	X 50	51	CAPACITY 52–55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
CA16	IOC	ACRYLONITRILE	SIC. NO. : COLS. 1-4 — X 2818
DATE PREPARED	PROCESS NITRIC OXIDE OXIDATION OF PROPYLENE	SOURCE	PRODUCT : COLS. 5-8 — X 1146
11-19-71		ABSORBER	PROCESS : COLS. 9-13 — 63
			SOURCE : COLS. 14-17 — X 1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
C_3H_6	5.4	C

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO 18	CNO 20 21	23 24	UNCON EMISS 30	Q 31	CEF 32	35	Q 36	SCF 37	40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

3. Industrial Inorganic Chemicals,Not Elsewhere Classified - SIC Industry No. 2819

Establishments primarily engaged in manufacturing industrial inorganic chemicals,not elsewhere classified. Important products of this industry include:

Inorganic salts
Inorganic compounds
Rare earth metal salts
Elements

Some of the nitro compounds of Industry No. 2819 include:

Ammonium compounds
Potassium compounds
Sodium compounds

For this study, these products were included:

Ammonium nitrate prills
Ammonium nitrate granules
Potassium nitrate
Sodium nitrite

The production of these four products consumes about 77 percent of the nitric acid production.

Product: Ammonium Nitrate Prills

Ammonium nitrate is made by the direct reaction between ammonia and nitric acid:

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

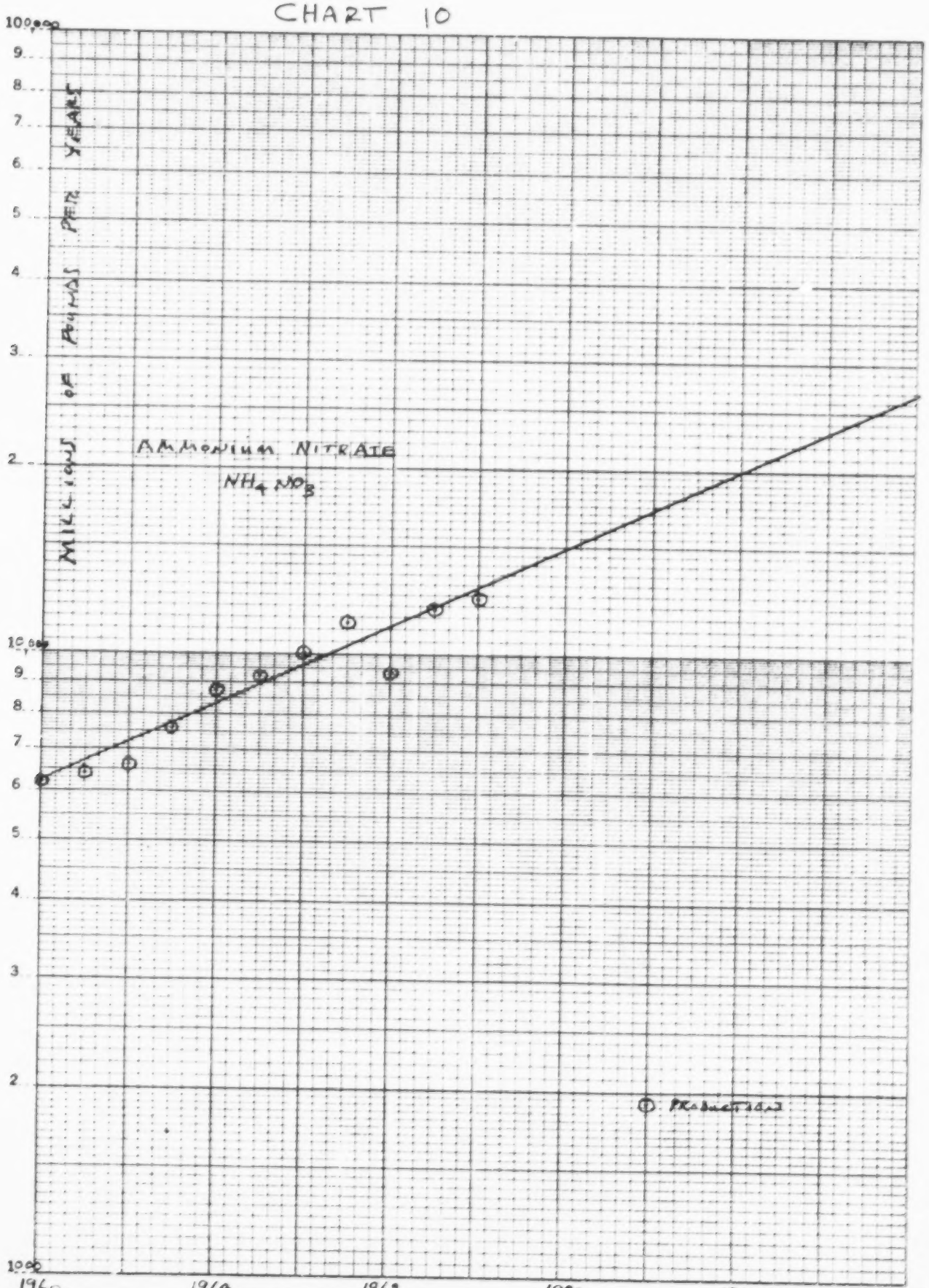
To make prills, the reaction is carried out in the liquid phase using water as the solvent. Part of the prill tower feed is sold directly as ammonium nitrate solution.

To make granules, the reaction is carried out in the vapor phase, producing liquid ammonium nitrate. This process is discussed elsewhere.

Ammonium nitrate is the largest consumer of nitric acid, using about 75 percent of the nitric acid production in 1970. Chart 10 shows a plot of the total production of ammonium nitrate. An annual growth rate of about 10 percent is expected. About 8 percent of the ammonium nitrate is made into granules, 41 percent into solution, and 51 percent into prills. Most ammonium nitrate plants are very flexible, being capable of producing a wide distribution of products.

Ammonium nitrate has two major uses. Over 90 percent is used as a fertilizer, and the remainder is used for explosives.

CHART 10



K•E LOGARITHMIC 3 CYCLES X 70 DIVISIONS KEUFFEL & ESSER CO. ~3 48

Process: Nitration of Ammonia to Ammonium Nitrate Prills

a. Feed Preparation

None.

b. Reaction Conditions

Ammonia gas is reacted with a slight excess of nitric acid as a liquid at 50 to 80C and atmospheric pressure. The reaction is exothermic. The heat of reaction is used to evaporate a portion of the water which is present to give an 83 percent ammonium nitrate solution from the reactor. The process yield is 98 percent.

c. Product Purification

No product purification is required. However, additional process steps are necessary after the reaction step.

The 83 percent ammonium nitrate solution is sold for fertilizer, or it is further concentrated to 93 percent ammonium nitrate solution and sold.

If a prilled product is desired, the 83 percent ammonium nitrate from the reactor is concentrated in one or two stages of evaporation to produce a 95 to 97 percent solution. This solution is fed hot to a prilling tower. The product from the prilling tower is screened, dried to less than 0.5 percent moisture, cooled, and rescreened. The final screened product is coated to prevent caking and deterioration in storage. The product purity is 99 percent before coating.

d. Recycle Systems

The oversize and undersize materials from the screening operations are dissolved in water and are recycled to the reactor.

All equipment in the dry solids handling steps is vented to a water scrubber to recover any product which is present. The water from the scrubber is combined with the solids and recycled to the reactor.

e. Raw Materials

The raw materials used in the process are 50 to 60 percent nitric acid, anhydrous ammonia, and the coating material (such as diatomaceous earth).

f. By-products

There are no by-products.

g. Sources of Air Pollution

There are three primary vents in the process. Two of these have a single control device. These are the vent from the reactor, which contains steam and acid fumes, and the vent collection system from the dry product handling equipment. These vents pass through a common scrubber before discharge to the atmosphere. The third vent is from the prilling tower and contains air and product particulates.

PR 109

FLOW DIAGRAM
AMMONIUM NITRATE MANUFACTURE

Job EPA

Location

Subject NITRATION STUDY

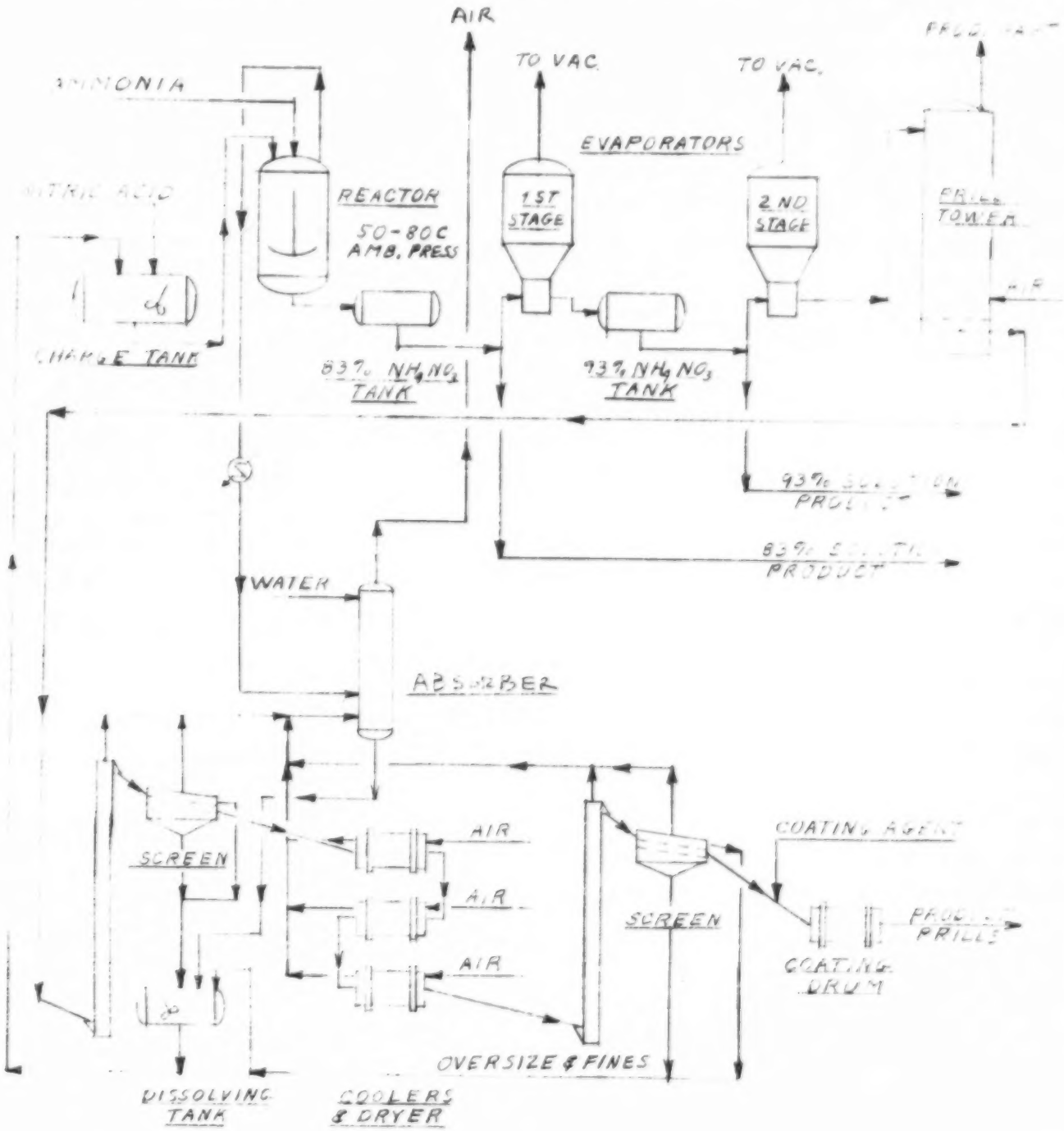
PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

File No 3382 Sheet No

Checked by Date

Computed by GNT Date 6-20-

PROCESS: DIRECT REACTION - PRILL (AND SOLUTION) PROCESS



PROCESS DATA TABULATION

SH____OF____

SIC. NO.	INDUSTRY	PRODUCT
2819	IIC	AMMONIUM NITRATE

DATE:	PROCESS
11-15-71	NITRATION OF AMMONIA

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	1	9
PRODUCT : COLS. 5-8	X		1	0	6
PROCESS : COLS. 9-13				1	3

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
	(SEE ATTACHED LIST)				

COMPUTER CODE NOS.

AQCR 19 22	STATE 23 24	CITY 25	26 27	COMPANY	CAPACITY 49 50 51 52	Q 55	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
		AMMONIUM NITRATE NH_4NO_3	SIC. NO. : COLS. 1-4
DATE PREPARED 10-11-71	PROCESS NITRIC ACID AMM AMMONIA	SOURCE	PRODUCT : COLS. 5-8
			PROCESS : COLS. 9-13
			QUALITY : COL 14

COMPUTER CODE NOS.

AOCR (19-22)	STATE (23-24)	CITY (25-36)	COMPANY (37-48)	CAPACITY (49-52)	Q (53)	YEAR (54-55)
131	NY	OLEAN	AGWAY	146	A	70
53	LA	GEISMER	ALLIED CH	500		70
145	VA	HOPEWELL	ALLIED CH	630		70
64	OH	IRONTON	ALLIED CH	600		70
50	NB	OMAHA	ALLIED CH	230		70
116	MO	HANNIBAL	AM CYANAMID	264		70
99	AZ	BENSON	APACHE POWDER	130		70
139	AR	HELENA	ARKLA CH.	210		70
118	MO	JOPLIN	ATLAS CH.	168		70
55	PA	TAMAQUA	ATLAS CH	84		70
UNC	LNB	FREMONT	CEN FARM FERT	78		70
218	IN	TERRE HAUTE	CEN NITROGEN	310		70
79	OK	PRYOR	CHEROKEE NIT	170		70
89	WY	CHEYENNE	WYCON CH	148		70
114	GA	AUGUSTA	COLUMBIA NIT	416		70

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
		AMMONIUM NITRATE NH_4NO_3	SIC NO. COLS. 1-4
DATE PREPARED	PROCESS	SOURCE	PRODUCT COLS. 5-8
10-11-71	NITRIC ACID AND AMMONIA		PROCESS COLS. 9-13
			QUALITY COL 14

COMPUTER CODE NOS.

ABCK	STATE	CITY	COMPANY	CAPACITY	Q	YEAR
22	CNB	BEATRICE	COMINCO AMER	340	A	70
UNC	LUT	COMEX	COMM. SOLV	2		70
2C	SILM	ARION	COMM SOLV	100		70
23	PASE	IPLE	COMM SOLV	10		70
UNC	LLA	STERLINGTON	COMM SOLV	374		70
25	IKS	LAWRENCE	COOP FARM. CH	540		70
66	WI	BARKSDALE	DU PONT	36	B	70
41	AL	BIRMINGHAM	DU PONT	60	A	70
187	WA	DU PONT	DU PONT	40		70
15	NJ	GIBBSTOWN	DU PONT	100		70
16	CO	LOUVIERS	DU PONT	36		70
2C	2IL	SENECA	DU PONT	394		70
18	FL	PENSACOLA	EBASCO	200		70
152	NC	TUNIS	FARMERS CH	400	B	70
120	TN	TYNER	FARMERS CH	400	B	70

(3)

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
		AMMONIUM NITRATE NH_4NO_3	SIC. NO. : COLS. 1-4
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8
	NITRIC ACID AND AMMONIA		PROCESS : COLS. 9-13
			QUALITY : COL. 14

COMPUTER CODE NOS.

AQCR (19-22)	STATE (23-24)	CITY (25-36)	COMPANY (37-49)	CAPACITY (50-55)	Q (56)	YEAR (57-58)
	18	MISSISSIPPORT	W R GRACE	58	A	70
	15	2NCWILMINGTON	W R GRACE	412		70
	11	HENDERSON	GULF OIL	200		70
	25	4KSPITTSBURG	GULF OIL	690		70
	12	2MSVICKSBURG	GULF OIL	60		70
	14	NCLIACLINTON	HAWKEYE CH	290		70
	41	ALBESSEMER	HERCULES	50		70
	11	8MOCARTHAGE	HERCULES			
	23	PADONORA	HERCULES	300		70
	17	CAHERCULES	HERCULES	160	B	70
	13	NJKENVIL	HERCULES	40	A	70
	11	CMOLOUISIANA	HERCULES	1000		70
	26	21LMARSEILLES	ILLNITROGEN	300		70
	23	8GABAINBRIDGE	KAISER	118		70
	20	CHNORTHBEND	KAISER	210		70

(1)

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
		AMMONIUM NITRATE NH_4NO_3	SIC. NO. : COLS. 1-4
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8
	NITRIC ACID AND AMMONIA		PROCESS : COLS. 9-12
			QUALITY : COL. 14

COMPUTER CODE NOS.

AOCR (19–22)	STATE (23–24)	CITY (25–36)	COMPANY (37–49)	CAPACITY (52–55)	Q (56)	YEAR (57–58)
1 1 3	GA	SAVANNAH	KAISER	904	A	70
9 6	FL	TAMPA	KAISER	104	A	70
4 1	AL	KETONA	KETONACHEM	96	B	70
1 3 4	TX	KERENS	LONESTAR	112	A	70
1 4 2	MS	YAZOOCITY	MISCO	600	A	70
5 2	TX	BEAUMONT	MOBIL	388		70
UNCL	AR	ELDORADO	MONSANTO	700		70
5 3	LA	LULING	MONSANTO	550		70
2 6 3	IL	TUSCOLA	NATDISTILLERS	80		70
9 6	FL	TAMPA	NITRAM	300		70
UNCL	IL	CORDOVA	NITRIN	240		70
3 2	WA	FINLEY	PHILLIPSPAC	108	B	70
2 2	NB	BEATRICE	PHILLIPSPET	142	A	70
1 3 4	TX	ETLER	PHILLIPSPET	368	B	70
3 8	TX	PASADENA	PHILLIPSPET	34	A	70

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
		AMMONIUM NITRATE NH_4NO_3	SIC. NO. : COLS. 1-4
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8
	NITRIC ACID AND AMMONIA		PROCESS : COLS. 9-13
			QUALITY : COL. 14

COMPUTER CODE NOS.

AGCR 19–22	STATE 23–24	CITY 25–36	COMPANY 37–49	CAPACITY 52–55	Q 56	YEAR 57–58
27	MN	PINEBEND	STPAULAMMONIA	400	A	70
51	OR	STHELENS	SHELLOIL	48		70
17	CA	VENTURA	SHELLOIL	48		70
20	OH	LIMA	SOLARNITROGEN	158		70
118	MO	JOPLIN	SOLARNITROGEN	300		70
98	IA	FTMADISON	STDOILCALIF	170		70
189	WA	KENNEWICK	STDOILCALIF	170		70
21	CA	RICHMOND	STDOILCALIF	90		70
101	IA	PORTNEAL	TERRA	298	B	70
14	IL	LLOCKPORT	TEXACO	200	A	70
17	CA	BREA	UNIONOIL	120		70
189	WA	PASCO	UNIONOIL	200		70
UNCL	UT	GENEVA	USSTEEL	200		70
72	AL	CHEROKEE	USSAGRICHEM	200		70
18	MO	CRYSTALCITY	USSAGRICHEM	200		70

6

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
		AMMONIUM NITRATE NH_4NO_3	SIC. NO. : COLS. 1-4
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8
	NITRIC ACID AND AMMONIA		PROCESS : COLS. 9-13
			QUALITY : COL. 14

COMPUTER CODE NOS.

AQCR 19–22	STATE 23–24	CITY 25–36	COMPANY 37–48	49–51	CAPACITY 52–55	Q 56	YEAR 57–58
167	CA	ELCENTRO	VALLEYNITRO		90	A	70
36	AZ	CURTISS	APACHEPOWDER		190	B	71
122	MS	YAZOOCITY	MISSISSIPPI		520	A	71
101	IA	PORTHEAL	TERRA		290	B	71
99	WY	CHEYENNE	WYCON		198	A	71

SOURCE DATA TABULATION

1 of 2

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2819	IIC	PRILLS OF AMMONIUM NITRATE	SIC. NO. : COLS. 1-4 — X 2 8 1 9
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8 — X 1 0 6
1-15-71	NITRATION OF AMMONIA	ABSORBER	PROCESS : COLS. 9-13 — 1 3
			SOURCE : COLS. 14-17 — X 1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	NIL	A
NH_3	NIL	A

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q

COMPUTER CODE NOS.

PNO 1-20	CNO 21-24	UNCON EMISS 25-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

2 of 2

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2819	ITC	PRILLS OF AMMONIUM NITRATE	SIC. NO. : COLS. 1-4 — 2819
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8 — 106
11/15/71	NITRATION OF AMMONIA	PRILL TOWER	PROCESS : COLS. 9-13 — 13
			SOURCE : COLS. 14-17 — 28

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
PARTICULATE	0.86	A

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO 18–20	CNO 21–23	UNCON EMISS 24–30	Q 31	CEF 32–35	Q 36	SCF 37–40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

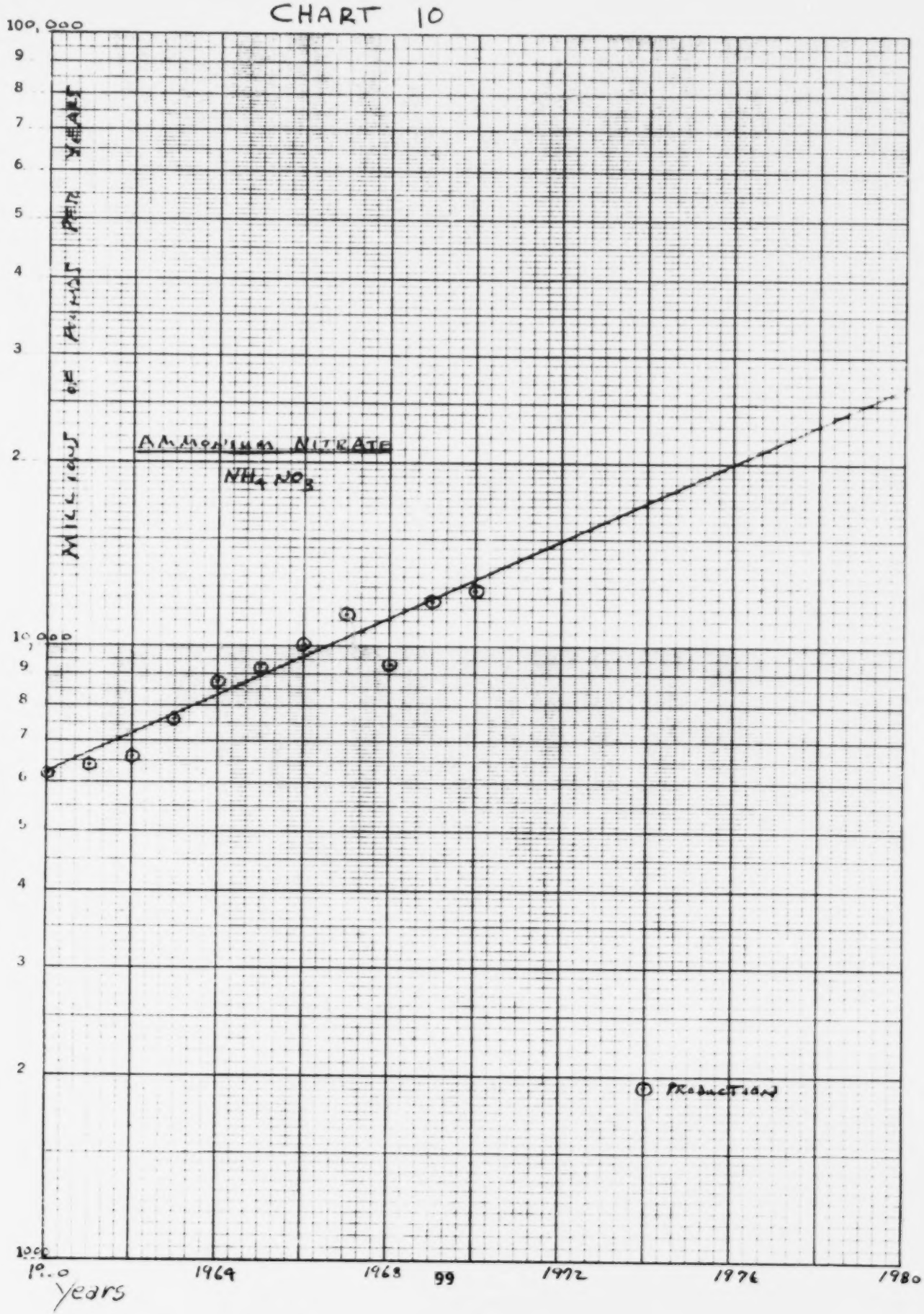
Product: Ammonium Nitrate Granules

Gaseous ammonia is reacted with vaporized nitric acid to produce, on cooling, granules of ammonium nitrate:

$$NH_3(g) + HNO_3(g) \longrightarrow NH_4NO_3(l)$$

About 8 percent of the total production of ammonium nitrate is made into granules or over a billion pounds in 1970. The main use of ammonium nitrate granules is for explosives. Chart 10 shows a plot of the total production of ammonium nitrate, which includes granules, prills and solution.

CHART 10


100,000
9
8
7
6
5
4
3
2
MILLIONS OF TONS PER YEAR
AMMONIUM NITRATE
NH_4NO_3
10,000
9
8
7
6
5
4
3
2
1000
① PRODUCTION
1960
1964
1968
1972
1976
1980
Years

Process: Nitration of Ammonia to Ammonium Nitrate Granules

a. Feed Preparation

None required.

b. Reaction Conditions

The process is known as the Stengel process. 50 to 60 percent nitric acid is vaporized and heated to 140 to 165C. The vapor is fed to the reactor where it mixes with ammonia which has been preheated to 145 to 150C before it is fed to the reactor. The reaction occurs as the mixture flows downward through vertical packed tubes. The temperature in the reactor rises to 200 to 240C as the reaction proceeds. The reactor pressure is 0 to 50 psig. The product out of the reactor is molten ammonium nitrate mixed with steam. This mixture passes to a separator where the molten ammonium nitrate drops out and flows downward through a packed section in the bottom of the separator. Air at 205C is fed to the separator below the packed section. This air flows upward through the separator and picks up the steam. The air and steam mixture flows out at the top of the separator to two condensers in series, where the steam condenses and any unreacted ammonia and entrained product particulates are absorbed in the condensate. The molten ammonium nitrate, containing less than 0.5 percent moisture, flows out of the bottom of the separator. The process yield is 98 percent.

c. Product Purification

No product purification is required. However, additional steps are required to obtain a granular product.

The molten ammonium nitrate from the separator is fed to a water-cooled belt where it freezes to a solid sheet. The solid sheet passes through a breaker as it leaves the belt. The solids are then ground and screened to obtain the desired product size. The product cut from screening is coated to prevent product caking and deterioration in storage. All equipment following the cooling belt is blanketed with controlled humidity air. This air is vented to a water scrubber, where entrained ammonium nitrate particles are removed. The solution from the scrubber is recycled to the reactor. The product purity is 99 percent before coating.

d. Recycle Systems

In addition to the liquid recycled from the scrubber to the reactor, the fines from screening and the liquid from the condensers are recycled to the reactor.

The oversize material from the screen is recycled to the grinder.

e. Raw Materials

The raw materials used are ammonia, 50 to 60 percent nitric acid, and the diatomaceous earth used as a product coating.

f. By-products

There are no by-products.

g. Sources of Air Pollution

There are two sources of air pollution. These are the vent from the condensers and the vent from the scrubber. Both of these vents emit air saturated with water vapor, and may contain product particulates.

PK 109

FLOW DIAGRAM
AMMONIUM NITRATE MANUFACTURE

Job EPA

Location

Subject NITRATION STUDY

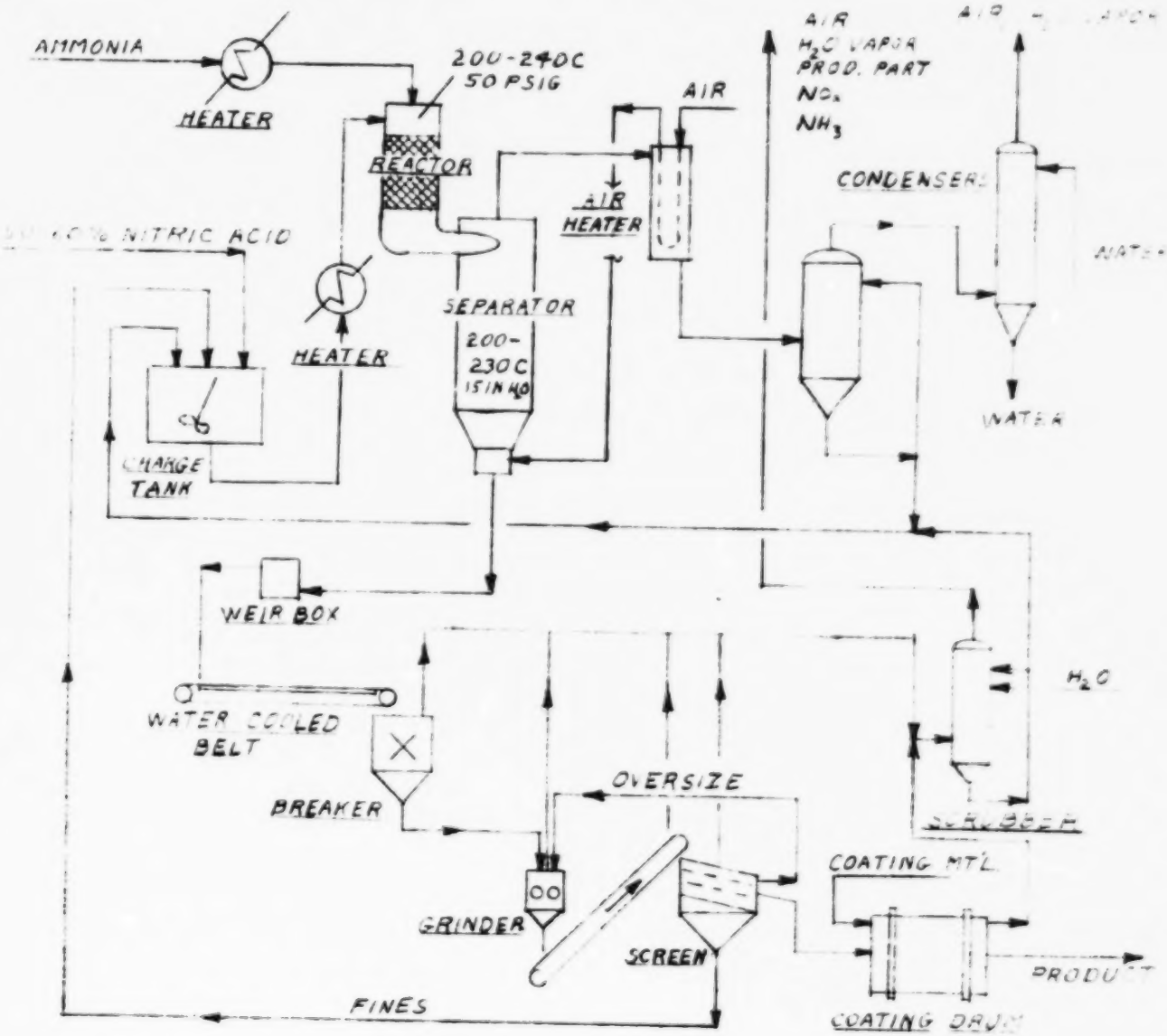
PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

File No 335 Sheet No

Checked by Date

Computed by G.V.T. Date 2-19-71

Process: DIRECT REACTION - GRANULE PROCESS



PROCESS DATA TABULATION

SH ____ OF ____

SIC NO.	INDUSTRY	PRODUCT
2819	IIC	AMMONIUM NITRATE

DATE:	PROCESS
11-15-71	NITRATION OF AMMONIA

COMPUTER CODE NOS.

SIC. NO. : COLS 1-4	X	2	8	1	9
PRODUCT : COLS 5-8	X		1	4	8
PROCESS : COLS 9-13				1	2

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
	(SEE ATTACHED LIST)				

COMPUTER CODE NOS.

AQCR 19–22	STATE 23–24	CITY 25–36	COMPANY 37–48	X 49	50–61	CAPACITY 62–66	Q 67	YEAR 68–69

MISCELLANEOUS

RELATED SIC. NOS:

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
		AMMONIUM NITRATE NH_4NO_3	SIC. NO. : COLS. 1-4
DATE PREPARED 10-11-71	PROCESS NITRIC ACID AMMONIA	SOURCE	PRODUCT : COLS. 5-8
			PROCESS : COLS. 9-13
			QUALITY : COL. 14

COMPUTER CODE NOS.

AQCR 19–22	STATE 23 24	CITY 25–36	COMPANY 37–49	>< 50 51	CAPACITY 52–55	Q 56	YEAR 57 58
131	NY	OLEAN	AGWAY		146	A	70
53	LA	GEISMER	ALLIED CH		500	A	70
145	VA	HOPEWELL	ALLIED CH		630	A	70
69	OH	IRONTON	ALLIED CH		600	A	70
50	NB	OMAHA	ALLIED CH		230	A	70
11	CM	OHANNIBAL	AM CYANAMID		264	A	70
99	AZ	BENSON	APACHE POWDER		130	A	70
139	AR	HELENA	ARKLA CH.		210	A	70
116	MO	JOPLIN	ATLAS CH.		168	A	70
55	PA	TAMAQUA	ATLAS CH		84	A	70
103	CL	NB FREMONT	CEN FARM FERT		78	A	70
218	IN	TERRE HAUTE	CEN NITROGEN		310	A	70
79	OK	PRYOR	CHEROKEE NIT		110	A	70
31	[illegible]	CHEYENNE	WYCON CH		148	A	70
11	GA	AUGUSTA	COLUMBIA NIT		416	A	70

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
		AMMONIUM NITRATE NH_4NO_3	SIC. NO. : COLS. 1-4
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8
10-11-71	NITRIC ACID AND AMMONIA		PROCESS : COLS. 9-13
			QUALITY : COL. 14

COMPUTER CODE NOS.

AQCR 19–22	STATE 23 24	CITY 25–36	COMPANY 37–49	CAPACITY 52–55	Q 56	YEAR 57 58
226	NB	BEATRICE	COMINCO AMER	340	A	70
UNCL	UT	COMEX	COMM. SOLV	8	A	70
265	IL	MARION	COMM SOLV	100	A	70
23	PA	SEIPLE	COMM SOLV	10	A	70
UNCL	LA	STERLINGTON	COMM SOLV	374	A	70
251	KS	LAWRENCE	COOP. FARM. CH	540	A	70
66	WI	BARKSDALE	DU PONT	36	B	70
41	AL	BIRMINGHAM	DU PONT	60	A	70
187	WA	DU PONT	DU PONT	40	A	70
15	NJ	GIBBSTOWN	DU PONT	100	A	70
16	CO	LOUVIERS	DU PONT	36	A	70
262	IL	SENECA	DU PONT	394	A	70
68	FL	PENSACOLA	EBASCO	200	A	70
152	NC	TUNIS	FARMERS CH.	400	B	70
120	TN	TYNER	FARMERS CH	400	B	70

(3)

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
		AMMONIUM NITRATE NH_4NO_3	SIC. NO. : COLS. 1-4
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8
	NITRIC ACID AND AMMONIA		PROCESS : COLS. 9-13
			QUALITY : COL. 14

COMPUTER CODE NOS.

AQCR 19–22	STATE 23 24	CITY 25–36	COMPANY 37–49	50 51	CAPACITY 52–55	Q 56	YEAR 57 58
180	ME	SEARSPORT	W R GRACE		58	A	70
152	NC	WILMINGTON	W R GRACE		412	A	70
61	KY	HENDERSON	GULF OIL		200	A	70
254	KS	PITTSBURG	GULF OIL		690	A	70
122	MS	VICKSBURG	GULF OIL		60	A	70
UP	CL	IACLINTON	HAWKEYE CH		290	A	70
41	AL	BESSEMER	HERCULES		50	A	70
118	MO	CARTHAGE	HERCULES		--	C	--
23	PA	DONORA	HERCULES		300	A	70
17	CA	HERCULES	HERCULES		160	B	70
13	NJ	KENVIL	HERCULES		40	A	70
11	LC	MOLOUISIANA	HERCULES		1000	A	70
262	IL	MARSEILLES	ILLNITROGEN		300	A	70
238	GA	BAINBRIDGE	KAISER		118	A	70
200	HN	ORTHBEND	KAISER		210	A	70

(4)

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
		AMMONIUM NITRATE NH_4NO_3	SIC. NO. : COLS. 1-4
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8
	NITRIC ACID AND AMMONIA		PROCESS : COLS. 9-13
			QUALITY : COL. 14

COMPUTER CODE NOS.

AQCR 19–22	STATE 23–24	CITY 25–36	COMPANY 37–48	49	50–51	CAPACITY 52–55	Q 56	YEAR 57–58
113	GA	SAVANNAH	KAISER			904	A	70
96	FL	TAMPA	KAISER			104	A	70
41	AL	KETONA	KETONACHEM			96	B	70
134	TX	KERENS	LONESTAR			112	A	70
122	MS	YAZOOCITY	MISCO			600	A	70
52	TX	BEAUMONT	MOBIL			388	A	70
UNCL	AR	ELDORADO	MONSANTO			700	A	70
53	LA	LULING	MONSANTO			550	A	70
263	IL	TUSCOLA	NATDISTILLERS			80	A	70
96	FL	TAMPA	NITRAM			300	A	70
UNCL	IL	CORDOVA	NITRIN			240	A	70
32	WA	FINLEY	PHILLIPSPAC			108	B	70
22	CN	BEATRICE	PHILLIPSPET			142	A	70
134	TX	ETLER	PHILLIPSPET			368	B	70
38	TX	PASADENA	PHILLIPSPET			34	A	70

PAGE 3

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
		AMMONIUM NITRATE NH_4NO_3	SIC. NO. : COLS. 1-4
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8
	NITRIC ACID AND AMMONIA		PROCESS : COLS. 9-13
			QUALITY : COL. 14

COMPUTER CODE NOS.

AQCR 19-22	STATE 23-24	CITY 25-36	COMPANY 37-49	50-51	CAPACITY 52-55	Q 56	YEAR 57-58
	27	MN PINEBEND	STPAULAMMONIA		400	A	70
	51	ORSTHELENS	SHELLOIL		48	A	70
	17	CAVENTURA	SHELLOIL		48	A	70
	20	OHLIMA	SOLARNITROGEN		158	A	70
	18	MOJOPLIN	SOLARNITROGEN		300	A	70
	98	AFTMADISON	STDOILCALIF		170	A	70
	37	WAKENNEWICK	STDOILCALIF		170	A	70
	01	CARICHMOND	STDOILCALIF		90	A	70
	01	IAPORTNEAL	TERRA		298	B	70
	14	LLSCAPORT	TEXACO		200	A	70
	01	CABREA	UNIONOIL		120	A	70
	37	WAPASCO	UNIONOIL		200	A	70
		UTSENIA	USSTEEL		200	A	70
	12	ALCHEMOKEE	USSAGRICHEM		200	A	70
		YSTALCITY	USSAGRICHEM		200	A	70

6

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
		AMMONIUM NITRATE NH_4NO_3	SIC. NO. : COLS. 1-4
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8
	NITRIC ACID AND AMMONIA		PROCESS : COLS. 9-13
			QUALITY : COL. 14

COMPUTER CODE NOS.

AQCR 19–22	STATE 23–24	CITY 25–36	COMPANY 37–49	50–51	CAPACITY 52–55	Q 56	YEAR 57–58
101	CA	EL CENTRO	VALLEY NITRO		90	A	70
3C	AL	COUNTISS	APACHE POWDER		190	B	71
122	MS	YAZOO CITY	MISSISSIPPI		520	A	71
101	IA	PORTHEAL	TERRA		290	B	71
8C	WY	CHEYENNE	WYCON		148	A	71

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2819	IIC	GRANULES OF AMMONIUM NITRATE	SIC. NO. : COLS. 1-4 — X 2819
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8 — X 148
11-15-71	NITRATION OF AMMONIA	CONDENSER	PROCESS : COLS. 9-13 — 12
			SOURCE : COLS. 14-17 — X 39

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	NIL	A
NH_3	NIL	A

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				
"				

COMPUTER CODE NOS.

PNO 18–20	CNO 21–23	UNCON EMISS 24–30	Q 31	CEF 32–35	Q 36	SCF 37–40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

2.02

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2819	IIC	GRANULES OF AMMONIUM NITRATE	SIC. NO. : COLS. 1-4 — 2819
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8 — 148
11-15-71	NITRATION OF AMMONIA	COOLER AND SCREEN	PROCESS : COLS. 9-13 — 12
			SOURCE : COLS. 14-17 — 8

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	1.3	A
NH_3	0.7	A
PARTICULATE	3.5	A

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
WET SCREEN SCRUBBER	0.95	A	1.0	B
"	0.96	A	"	B
"	0.95	A	"	B

COMPUTER CODE NOS.

PNO 18–20	CNO 21–23	UNCON EMISS 24–30	Q 31	CEF 32–36	Q 37	SCF 37–40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Potassium Nitrate

There is one plant in the United States reacting potassium chloride with nitric acid in a two step process:

$$3KCl + 4HNO_3 \longrightarrow 3KNO_3 + NOCl + Cl_2 + 2H_2O$$

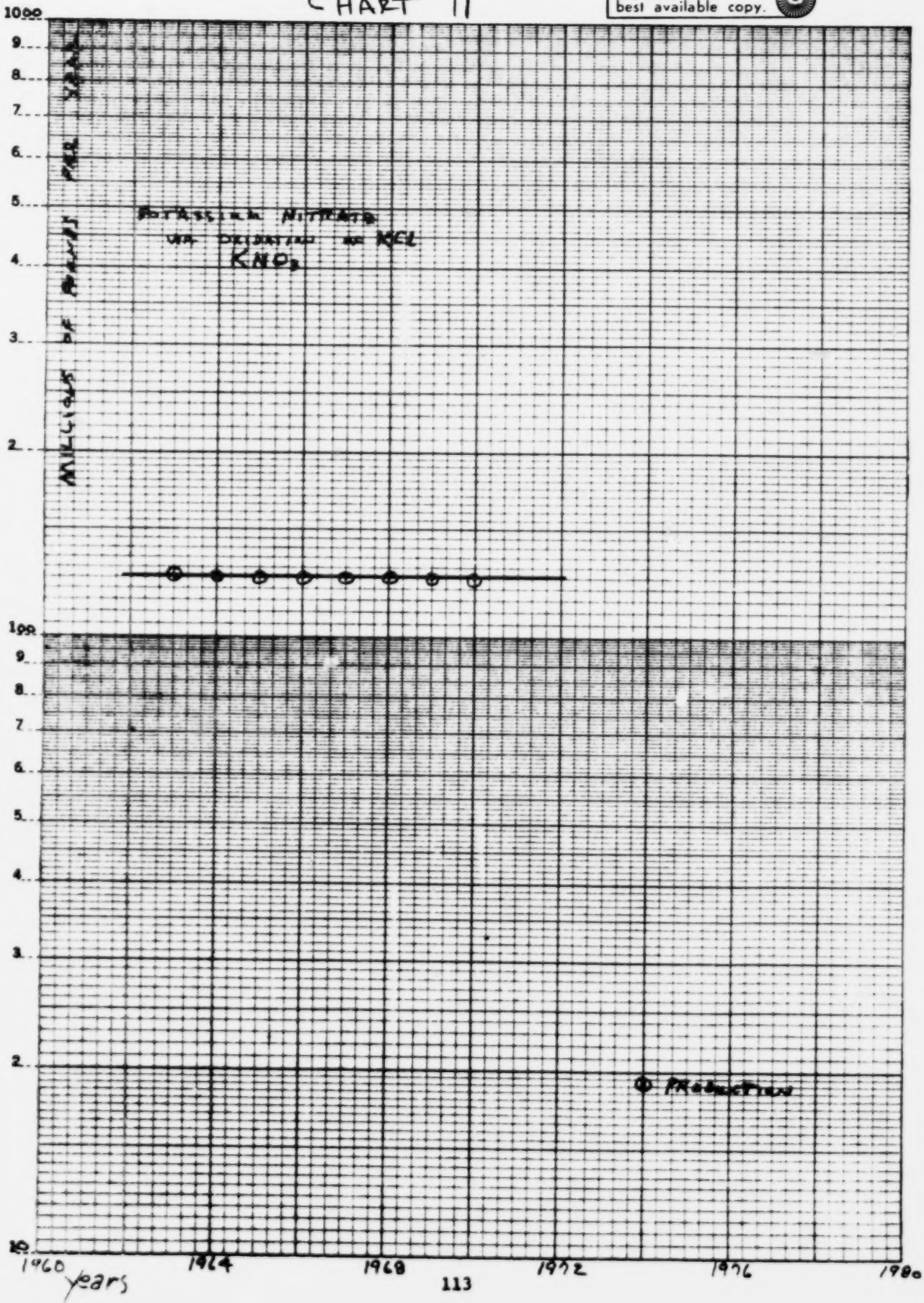
$$2NOCl + 4HNO_3 \longrightarrow Cl_2 + 6NO_2 + 2H_2O$$

The plant which started production in 1962 produces 126 million pounds of KNO_3 and 59 million pounds of Cl_2 per year. No expansion of the process is expected. See Chart 11 for plot of data.

The KNO_3 is used as a fertilizer, and Cl_2 is sold as a valuable by-product.

Reproduced from best available copy.

CHART 11



Process: Oxidation of Potassium Chloride for Chlorine and Potassium Nitrate

a. Feed Preparation

Solid potassium chloride is mixed with 65 percent nitric acid and the mixture is fed to the reactor. The nitric acid is chilled to below 10C before the mixing operation to minimize the reaction until the mixture is in the reactor. The potassium chloride-nitric acid mixture enters the reactor through a seal leg to prevent blow back, since the reactor operates above atmospheric pressure.

b. Reaction Conditions

The reaction system consists of three steps. These are the reactor, which is an agitated tank, the muriate reactor, which is a column and has a combination of valve and sieve trays, and the gas reactor, which is also a column and is made of glass-lined steel. The reaction system operates at 20 psig. The temperature is not known.

The initial reaction ($3KCl + 4HNO_3 \longrightarrow 3KNO_3 + NOCl + Cl_2 + 2H_2O$) starts in the reactor and goes to completion in the muriate reactor. An excess of nitric acid is used.

A HNO_3 heater and vaporizer produces hot nitric acid liquid, which is fed to the reactor in order to promote the reaction, and nitric acid vapor, which is fed to the bottom of the muriate column to strip the chlorine and chlorides from the HNO_3-KNO_3 solution down to 0.004 percent or less. The bottoms from the muriate reactor column, a mixture of HNO_3 and KNO_3, contains the desired potassium nitrate, and goes to the water stripper. The overheads are returned to the reactor.

The gas stream from the reactor goes to the gas reactor column where the second main reaction ($NOCl + 2HNO_3 \longrightarrow 3NO_2 + 1/2\ Cl_2 + H_2O$) occurs. A HNO_3 concentration above 70 percent is required. The reflux condenser on this column keeps nitric acid and water out of the overhead product. The bottoms stream from the gas reactor column is returned to the reactor. The overheads stream is totally condensed and is fed to the Cl_2 still.

No information is available on process yields.

c. Product Purification

The HNO_3/KNO_3 solution from the bottom of the muriate column is fed to the water stripper. The water stripper works in conjunction with the KNO_3 saturator to increase the concentration of KNO_3 in the water stripper. This shifts the azeotrope concentration to produce a stronger HNO_3. The overheads from the water stripper go to the water rectifier where water is removed overhead as a waste. The bottoms product is 65 percent HNO_3, which is recycled to the reactor. The bottoms from the water stripper go to the vacuum crystallizers where the kNO_3 crystallizes out. The overhead vapor is condensed and fed to a separator.

The slurry from the crystallizers is centrifuged. The mother liquor is returned to the crystallizers. The crystals are dried in a direct-fired dryer to produce technical grade potassium nitrate. The product purity is about 95 percent.

A prilled product of 99.3 percent purity can be produced by removing the slurry from the first stage of the evaporator (as shown by dotted

lines on the flow diagram). This slurry is centrifuged. The crystals are dried and then melted. The melt is fed to a prill tower. The prills are cooled to yield the 99.3 percent purity prilled product.

A second product (or a by-product) results from this process. This is liquid Cl_2 with a purity of 99.5 percent. This is obtained by distillation at 40 psig in the Cl_2 still of the overhead product from the gas reactor column. The bottoms from the Cl_2 still is fed to the N_2O_4 still.

d. Recycle Systems

There are several recycle systems in addition to the recycles between the reaction columns and the reactor (discussed under reaction conditions), the recycle from the water rectifier (discussed under product purification), and the recycle of the mother liquor from the centrifuge (also discussed under product purification).

The condensed vapor from the vacuum crystallizers goes to a separator. This is a nitric acid solution. The liquid phase goes back to the gas reactor column, while the vapors return to the water rectifier.

The bottoms from the Cl_2 still contain NO_2Cl, NOCl, BrCl and N_2O_4. This is fed to the N_2O_4 still. A bleed stream from the overheads of this still is fed to the BrCl still where the BrCl is concentrated in the overheads and goes to a scrubber where it is neutralized with caustic. The water solution from the scrubber is a waste product. The scrubber is vented to atmosphere. The bottoms from the BrCl still are returned to the N_2O_4 column.

The main overhead product from the N_2O_4 column contains NOCl and NO_2Cl plus N_2O_4, Cl_2, and BrCl. This is returned to the gas reactor column for oxidation with nitric acid in accordance with the second main reaction.

The bottoms from the N_2O_4 still is primarily N_2O_4. This goes to an agitated reactor tank where it is mixed with 55 percent HNO_3 and air to cause the regeneration reaction ($2NO_2 + H_2O + 1/2\ O_2 \longrightarrow 2HNO_3$) to take place. The liquids and unreacted N_2O_4 (NO_2) goes to a two-stage HNO_3 absorption column system, where the regeneration reaction is continued by the addition of more air. This absorption system produces a 65 percent nitric acid solution which is recycled to the reaction steps. The off gases from the HNO_3 absorber system, containing air and unabsorbed oxides of nitrogen, are vented.

e. Raw Materials

There are two raw materials, 55 percent nitric acid and solid potassium chloride.

f. By-products

There is one by-product. This is liquid chlorine with a purity of 99.5 percent.

g. Sources of Air Pollution

There are five sources of air pollution. The vent from the scrubber in which BrCl is absorbed and neutralized may contain BrCl and oxides of nitrogen. The vent from the HNO_3 absorber system will be primarily air with traces of unabsorbed oxides of nitrogen. The product dryer is direct fired and, therefore, it will vent combustion gases and some product particulates. The prill tower will vent air and some product particulates, as will the cooler following the prill tower.

FR 109

FLOW DIAGRAM
POTASSIUM NITRATE MANUFACTURE

Job EPA

Location

Subject NITRATION STUDY

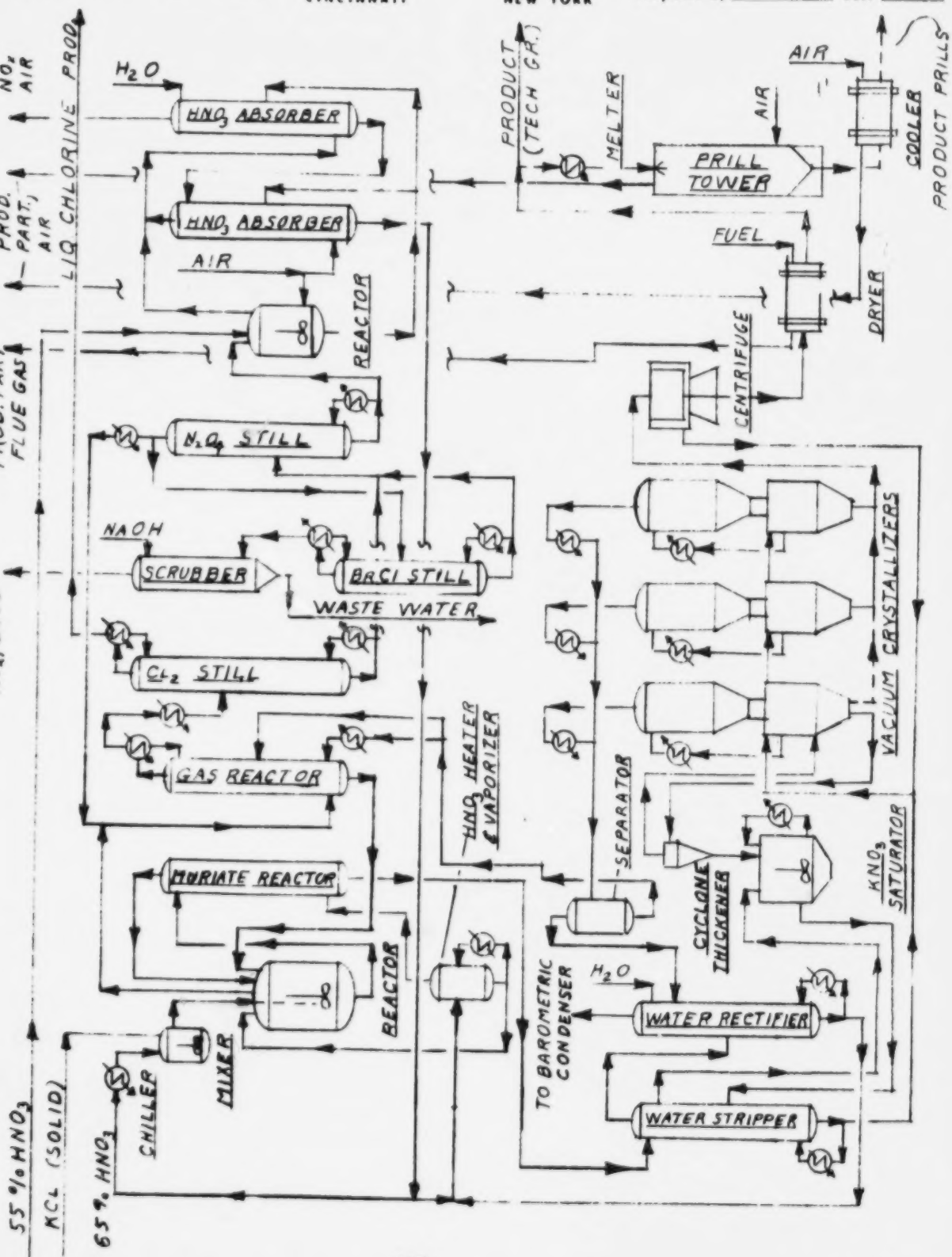
PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

File No 3382 Sheet No

Checked by Date

Computed by G.N.T. Date 11-2-71

PROCESS: NITRATION OF POTASSIUM CHLORIDE WITH NITRIC ACID



Q.a

PROCESS DATA TABULATION

SH____OF____

SIC. NO.	INDUSTRY	PRODUCT
2819	IIC	POTASSIUM NITRATE

DATE:	PROCESS
11-19-71	OXIDATION OF POTASSIUM CHLORIDE

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	1	9
PRODUCT : COLS. 5-8	X		1	4	4
PROCESS : COLS. 9-13				6	2

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
122	AMAX CHEMICAL	VICKSBURG, MS	A	12C	B

COMPUTER CODE NOS.

AQCR 19–22	STATE 23 24	CITY 25–36	COMPANY 37–49	X 50 51	CAPACITY 52–55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2819	IIC	POTASSIUM NITRATE	SIC. NO. : COLS. 1-4 X 2819
DATE PREPARED 11-17-71	PROCESS OXIDATION OF POTASSIUM CHLORIDE	SOURCE ABSORBER (HNO_3)	PRODUCT : COLS. 5-8 X 144
			PROCESS : COLS. 9-13 62
			SOURCE : COLS. 14-17 X 1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	0.08	C

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

2.5

INDUSTRY NO.	INDUSTRY	PRODUCT
2819	IIC	POTASSIUM NITRATE
DATE PREPARED	PROCESS	SOURCE
11-17-71	OXIDATION OF POTASSIUM CHLORIDE	ABSORBER No. 2 ($BrCl$)

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	1	9
PRODUCT : COLS. 5-8	X		1	4	4
PROCESS : COLS. 9-13				6	2
SOURCE : COLS. 14-17	X				5

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
$BrCl$	0.001	B

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO 18–20	CNO 21–23	UNCON EMISS 24–30	Q 31	CEF 32–35	Q 36	SCF 37–40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE	

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

3 of 5

INDUSTRY NO.	INDUSTRY	PRODUCT
2819	IIC	POTASSIUM NITRATE
DATE PREPARED	PROCESS	SOURCE
11-19-71	OXIDATION OF POTASSIUM CHLORIDE	DRYER

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	1	9
PRODUCT : COLS. 5-8	X		1	4	4
PROCESS : COLS. 9-13				6	2
SOURCE : COLS. 14-17	X			1	1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
PARTICULATE	1.8	B

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE	

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

4 of 5

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2819	IIC	POTASSIUM NITRATE	SIC. NO. : COLS. 1-4 X 2819
DATE PREPARED 11-17-71	PROCESS OXIDATION OF POTASSIUM CHLORIDE	SOURCE PRILL TOWER	PRODUCT : COLS. 5-8 X 144
			PROCESS : COLS. 9-13 62
			SOURCE : COLS. 14-17 X 28

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
PARTICULATE	0.86	B

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

5.0.5

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2819	IIC	POTASSIUM NITRATE	SIC. NO. : COLS. 1-4 X 2819
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8 X 1144
11-17-71	OXIDATION OF POTASSIUM CHLORIDE	COOLER	PROCESS : COLS. 9-13 62
			SOURCE : COLS. 14-17 X 6

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
PARTICULATES	10.2	B

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE	

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

Product: Sodium Nitrite

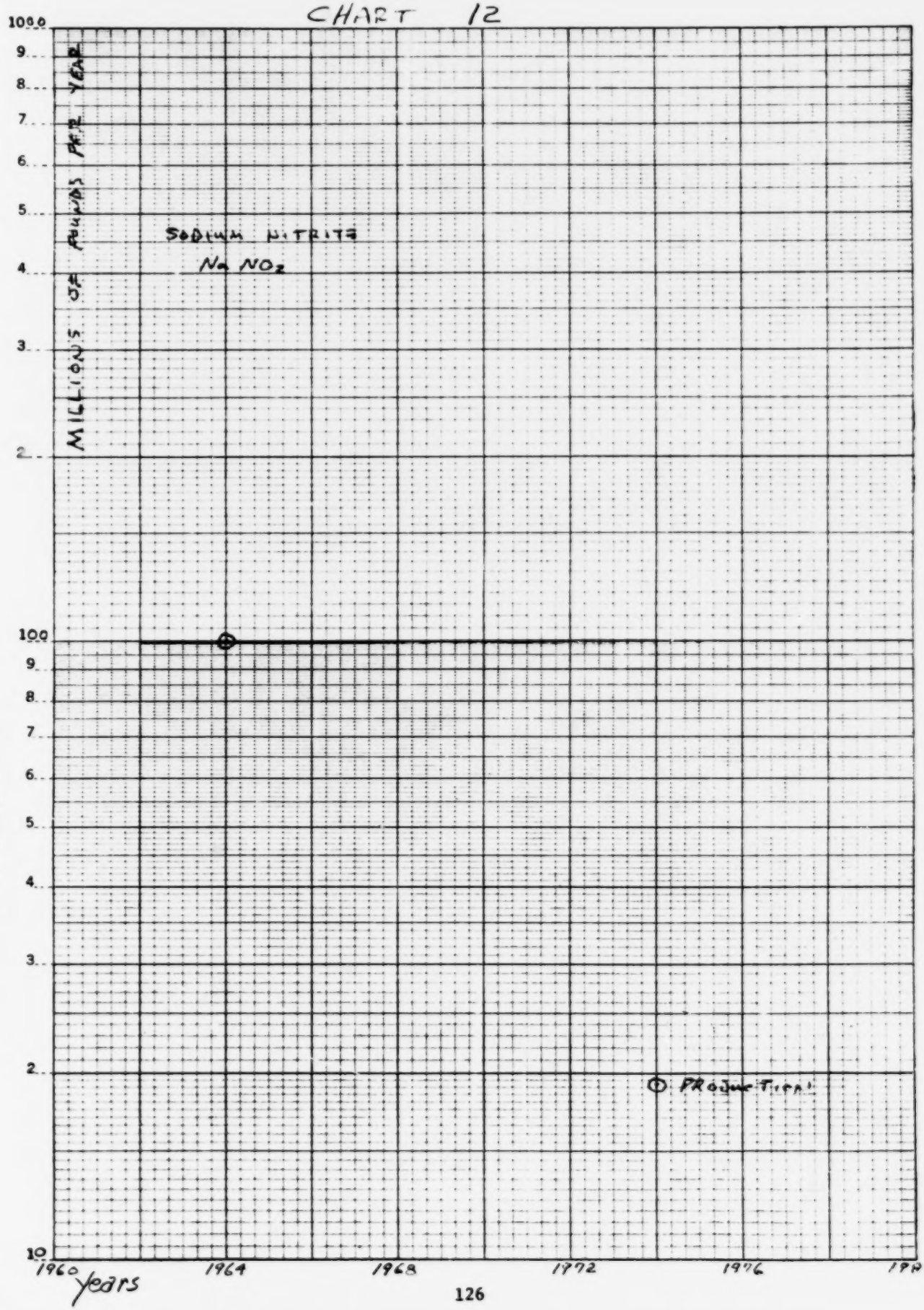
Sodium nitrite is made by reacting nitric oxide with sodium carbonate under oxidizing conditions:

$$2NO + Na_2CO_3 + 1/2\ O_2 \xrightarrow{(Air)} 2NaNO_2 + CO_2$$

There is little production data. Chart 12 shows a plot of the only point. Little growth is expected.

The main use of sodium nitrite is as a corrosion inhibitor for iron and steel. About 15 percent is used to produce azo dyes.

CHART 12



K•E SEMI-LOGARITHMIC 2 CYCLES X 60 DIVISIONS KEUFFEL & ESSER CO. 46 4853

Process: Oxidation of Sodium Carbonate to Sodium Nitrite

a. Feed Preparation

A solution of about 21 percent sodium carbonate is prepared by dissolving solid sodium carbonate in water.

Nitric oxide gas (NO) is obtained by catalytic oxidation of ammonia (NH_3) with air. This reaction is the same as for nitric acid manufacture; however, the secondary air is carefully controlled to give a ratio of NO/NO_2 in the product gas so that a minimum of $NaNO_3$ is produced in the reaction step.

b. Reaction Conditions

The process is either batch or continuous. For a continuous process, several absorption towers are operated in series. The description of a three-stage reactor follows.

The 21 percent sodium carbonate solution is fed to the third absorber in the series, and after passing through that absorber, it is transferred to, and passes through, the second absorber. Additional sodium carbonate may be added to the solution in the second stage to make up for that which has reacted. The solution is then sent to, and through, the first absorber and comes out with most of the sodium carbonate reacted. The NO gas plus air (or the $NO-NO_2$ gas mixture from the catalytic oxidation of ammonia) is fed to the bottom of the first absorber. It passes up through the first absorber and out the top, and then to the bottom of the second absorber. The gases pass through the second absorber and on to, and through, the third absorber in the same manner as for the first absorber. The gases from the third absorber are vented.

As the gases pass through the absorber, the NO and oxygen (or NO_2) react with the sodium carbonate to form sodium nitrite ($NaNO_2$) and carbon dioxide (CO_2).

The liquid from the bottom of the first absorber may contain 25 percent sodium nitrite, 5 percent sodium nitrate, and 0.5 percent sodium carbonate. It is transferred to a storage tank.

c. Product Purification

The liquor in the storage tank is transferred to the feed tank where it is blended with mother liquor from the first stage crystallization and redissolved crystals from the second evaporator.

A portion of the solution in the feed tank is fed to the first evaporator, while another portion is used to dissolve the crystals from the second stage evaporation (to be discussed later). In the evaporator, the solution is concentrated to about 50 percent sodium nitrite.

The solution from the evaporator passes to a vacuum crystallizer. The slurry from the vacuum crystallizer is filtered. The mother liquor from this filtration is split into three streams. About 10 percent is returned to the evaporator feed tank, about 45 percent goes back to the first stage absorber and about 45 percent goes to a second evaporator.

The filter cake from the above filtration is dried and becomes the sodium nitrite product.

In the second evaporator, the solution is concentrated to about 50 percent of the original volume. This concentration crystallizes out sodium nitrite. This slurry is filtered.

The filter cake from the second evaporator is high in sodium nitrite. It is redissolved in solution from the first evaporator feed tank. The resulting solution is sent back to the first evaporator feed tank.

d. Raw Materials

The raw materials for the process consist of sodium carbonate and either NO gas or an $NO-NO_2$ mixed gas from the controlled catalytic oxidation of ammonia.

e. By-products

The mother liquor from the second filtration is dried and ground to become a by-product containing about 55 percent sodium nitrite and 40 percent sodium nitrate.

f. Sources of Air Pollution

There are two sources of air pollution. The vent on the third absorber will contain air, carbon dioxide and unabsorbed oxides of nitrogen. The vent from the drum dryer will contain air, water vapor, and product particulates.

FR 109

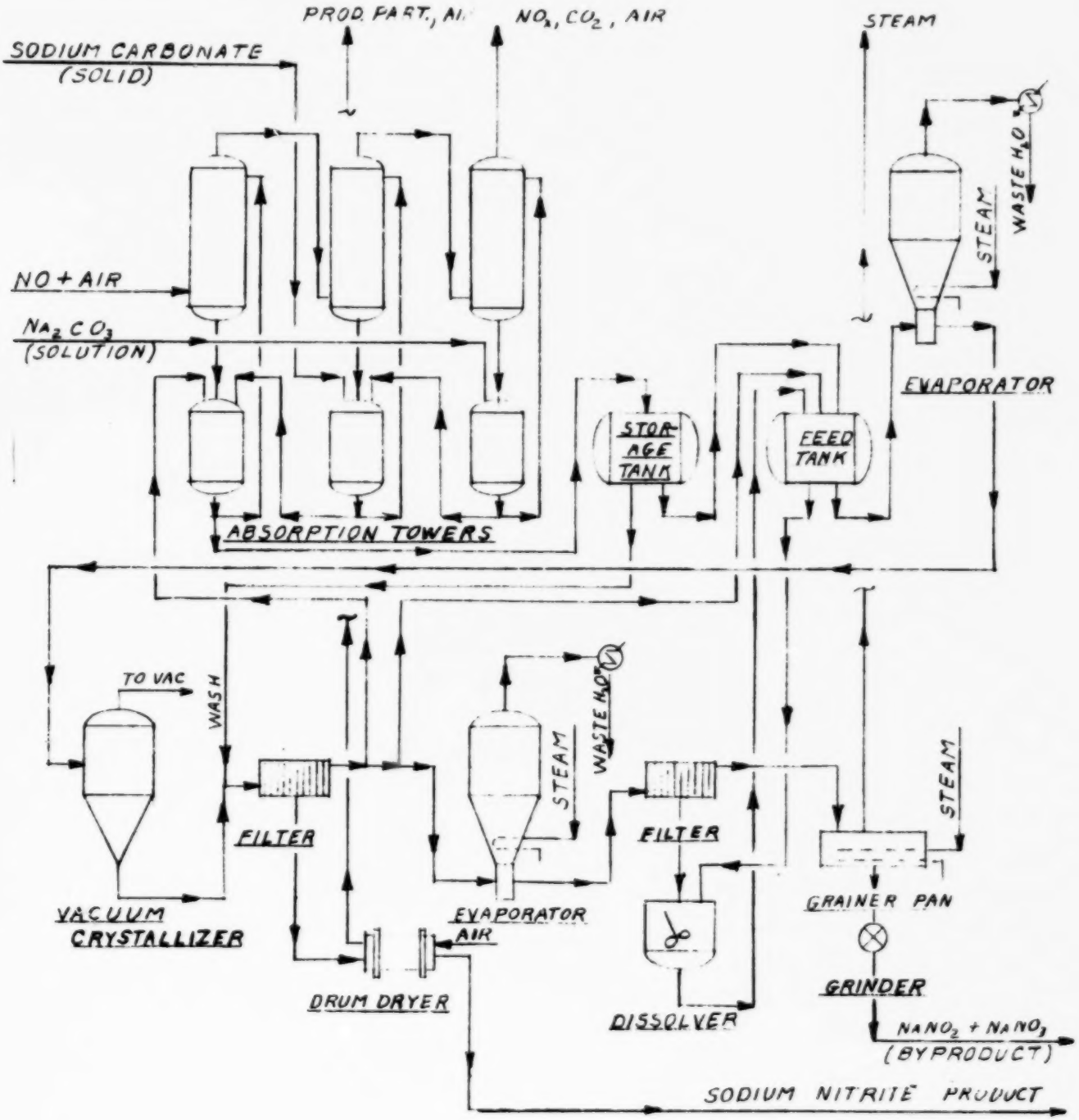
FLOW DIAGRAM
SODIUM NITRITE MANUFACTURE

Job EPA — **PROCESSES RESEARCH, INC.** — File No 3382 Sheet No ____

Location ____ — INDUSTRIAL PLANNING AND RESEARCH — Checked by ____ Date ____

Subject NITRATION STUDY — CINCINNATI NEW YORK — Computed by G.N.T. Date 11-2-71

PROCESS: NO PLUS AIR, REACTION WITH SODIUM CARBONATE



Q-1

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2819	IIC	SODIUM NITRITE

DATE:	PROCESS
11-17-91	OXIDATION OF SODIUM CARBONATE

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	1	9
PRODUCT : COLS. 5-8	X		1	4	7
PROCESS : COLS. 9-13				6	4

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
15	ALLIED	MARCUS HOOK, PA	A		
15	DUPONT	GIBBSTOWN, NJ	A		
18	MALLINCKRODT	SAINT LOUIS, MO	A		

COMPUTER CODE NOS.

AQCR 19–22	STATE 23 24	CITY 25–36	COMPANY 37–48	X 49	50 51	CAPACITY 52–55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

1 of 2

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2819	IIC	SODIUM NITRITE	SIC. NO. : COLS. 1-4 — X 2 8 1 9
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8 — X 1 4 7
11-17-71	OXIDATION OF SODIUM CARBONATE	ABSORBER	PROCESS : COLS. 9-13 — 6 4
			SOURCE : COLS. 14-17 — X 1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	NIL	A

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE	

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

2 of 2

INDUSTRY NO.	INDUSTRY	PRODUCT
2819	IIC	Sodium Nitrite
DATE PREPARED	**PROCESS**	**SOURCE**
11-17-71	Oxidation of Sodium Carbonate	Dryer

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	1	9
PRODUCT : COLS. 5-8	X		1	4	7
PROCESS : COLS. 9-13				6	4
SOURCE : COLS. 14-17	X			1	1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
Particulate	1.8	C

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
None				

COMPUTER CODE NOS.

PNO 18–20	CNO 21–23	UNCON EMISS 24–30	Q 31	CEF 32–35	Q 36	SCF 37–40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

4. Explosives - SIC Industry No. 2892

Establishments primarily engaged in manufacturing explosives.

Some important nitro compounds of industry No. 2892 include:

Nitrocellulose
Nitroglycerin
Nitromannitol
Nitro starch
Nitro sugars
TNT

For this study, these three products have been included:

Nitroglycerine
Nitrocellulose
TNT

Product: Nitroglycerine

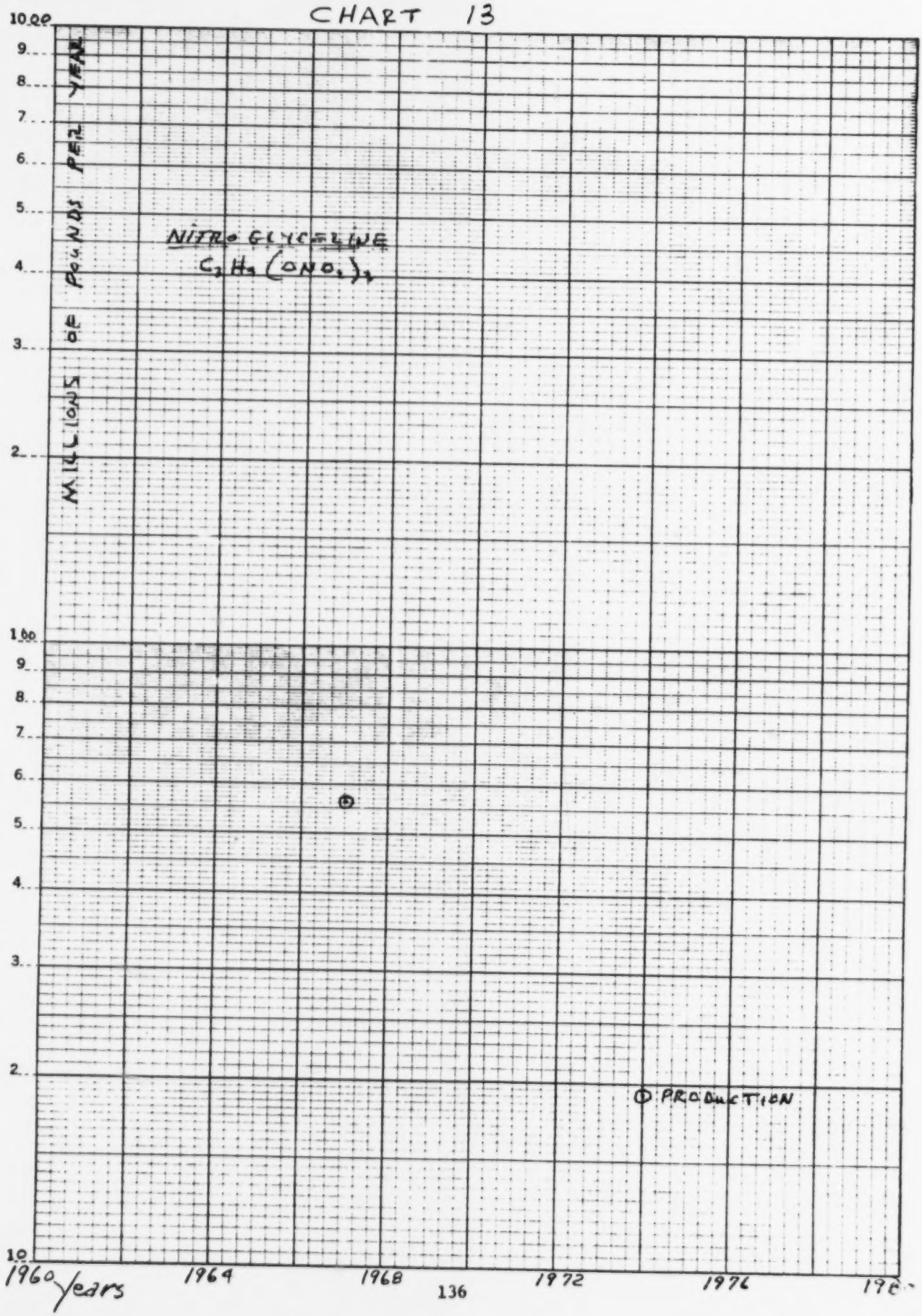
Nitroglycerine is an explosive which has been in commercial use for over 100 years. However, there is very little production data on it. See Chart 13 for industrial production. The main use of nitroglycerine is as an explosive.

Nitroglycerine is made by nitrating glycerine,

$$C_3H_3(OH)_3 + 3HONO_2 \longrightarrow C_3H_5(ONO_2)_3 + 3H_2O$$

Starting in the early Nineteen-fifties, nitroglycerine has been made in the United States by a continuous process, which has no NO_x emissions.

CHART 13


MILLIONS OF POUNDS PER YEAR
10.00
9
8
7
6
5
4
3
2
1.00
9
8
7
6
5
4
3
2
10
NITRO GLYCERINE
$C_3H_5(ONO_2)_3$
PRODUCTION
1960 years
1964
1968
1972
1976

Process: Nitration of Glycerine

a. Feed Preparation

A mixed acid is used for the nitration reaction. The composition is given as 49.5 percent H_2SO_4 and 52 percent HNO_3. This acid is prepared by mixing 60 percent oleum with 93 percent H_2SO_4 to produce a 40 percent oleum. This mixture is then mixed with 97 percent HNO_3 to give the desired mixed acid. The 97 percent HNO_3 is obtained by concentrating 50 to 60 percent HNO_3 in the acid concentration system.

b. Reaction Conditions

One of the continuous processes for making nitroglycerine is the Biazzi process. The nitrator has a capacity of about 32 gallons. It is uninsulated, has internal coils for cooling, and is equipped with an agitator. For emergency drowning there is a 6 inch opening in the bottom and a quick opening valve.

In operation, glycerine (and sometimes ethylene glycol) and mixed acid are fed separately to the nitrator. The mixed acid is fed to the surface of the liquid. The glycerine is fed below the surface. The reaction is controlled at about 15C when glycerine alone is fed. It is controlled at 12C when the feed is 50 percent ethylene glycol and 50 percent glycerine. The reaction product overflows continuously to the acid separator. The reactor is vented to an absorber. The process overall yield is 96 percent.

c. Product Purification

The reactor product is separated continuously in the acid separator, which is a specially designed centrifuge. The spent acid leaves the separator and goes to a dilution tank, where water is added at a rate of 2 percent of the acid flow to dissolve suspended nitroglycerine. Further processing of the spent acid is discussed under recycle systems.

The nitroglycerine liquid from the acid separation step goes to the washers, where it is washed with 13 percent sodium carbonate in water. The mixture of sodium carbonate, water and nitroglycerine overflows continuously from the first washer and through two additional washers in series to insure complete neutralization of any acid in the nitroglycerine. The washers are vented to the absorber.

The emulsion of nitroglycerine and soda water overflows the third washer and then flows by gravity through a pipe to a building where the soda water separator is located. Water is mixed with the emulsion as it enters the pipe through a break funnel. The water prevents deposition of salts in the soda separator. The break funnel serves to prevent transmission of an explosion in the soda water separator system to the reactor building. In the soda water separator, the neutralized salts and water are separated from the nitroglycerine and wasted. The nitroglycerine is jetted with water to the jet water separator. This system serves to water wash the nitroglycerine. The nitroglycerine then goes to storage for processing into dynamite.

d. Recycle Systems

There are two systems that can be called recycle systems. Both involve the waste acid.

The first system is not shown on the flow sheet, because it is used only on shutdown of the reactor. On shutdown, waste acid is caused to flow from a head tank into the bottom of the reactor (after the feeds have been shut off and agitation stopped). This waste acid displaces the nitroglycerine in the reactor, causing it to overflow to the acid separator. The overflow on the separator is adjusted so that the spent acid rises and pushes the last nitroglycerine out of the separator. (By means of bottom connections between the washers, they are emptied to the soda water separator.)

The other system treats the spent acid and the nitric acid from the absorber on the reactor and washer vents. This mixed acid is fed to the top of a denitrating tower which is heated with steam. As the spent acid flows down through the tower, it is stripped of HNO_3 and oxides of nitrogen by the vapors rising in the tower.

The gases from the top of the denitrating tower flow to the bleacher where they mix with air to oxidize any nitric oxide present. The gases flow upward and through a reflux condenser where any HNO_3 and H_2O condense and flow back to the bleacher and out as 97 percent nitric acid. This 97 percent acid goes to the mixed acid system, which is discussed under feed preparation. The off gases from the reflux condenser are fed to an absorption tower where additional oxidation of NO takes place, and the oxides of nitrogen are absorbed

in water and 50 to 60 percent nitric acid to form additional nitric acid. The bottoms from this absorber is fed to the top of the denitrating tower. All the makeup 50 to 60 percent nitric acid used in the process is fed either to the absorber or to the denitrating tower to be concentrated to 97 percent HNO_3.

The bottoms from the denitrating tower, which is 60 to 70 percent sulfuric acid, is fed to the sulfuric acid concentrator. In the sulfuric acid concentrator, water is removed from the H_2SO_4 and becomes a waste product. A 93 percent sulfuric acid solution is produced by the concentrator. Only a portion of this acid can be used in the mixed acid system. The excess 93 percent H_2SO_4 is sold as a by-product or becomes a waste stream.

e. Raw Materials

The major raw materials are 60 percent oleum, 50 to 60 percent nitric acid, glycerine, and, at some plants, ethylene glycol. A raw material used in lesser amounts is sodium carbonate.

f. By-products

The process produces one by-product. This is 93 percent sulfuric acid contaminated with nitrobodies.

g. Air Pollution Sources

There are two sources of air pollution. These are the vent from the absorber on the reactor vent and the vent on the absorber in the acid concentration system. Both vents will vent air and unabsorbed oxides of nitrogen, and HNO_3 fumes.

Some plants will have a third air pollution source, if a drum concentrator is used for sulfuric acid concentration. The vent from this will contain combustion gases, H_2SO_4 mist, and nitrobodies.

PR 109

FLOW DIAGRAM
NITROGLYCERINE MANUFACTURE

Job E.P.A.

Location

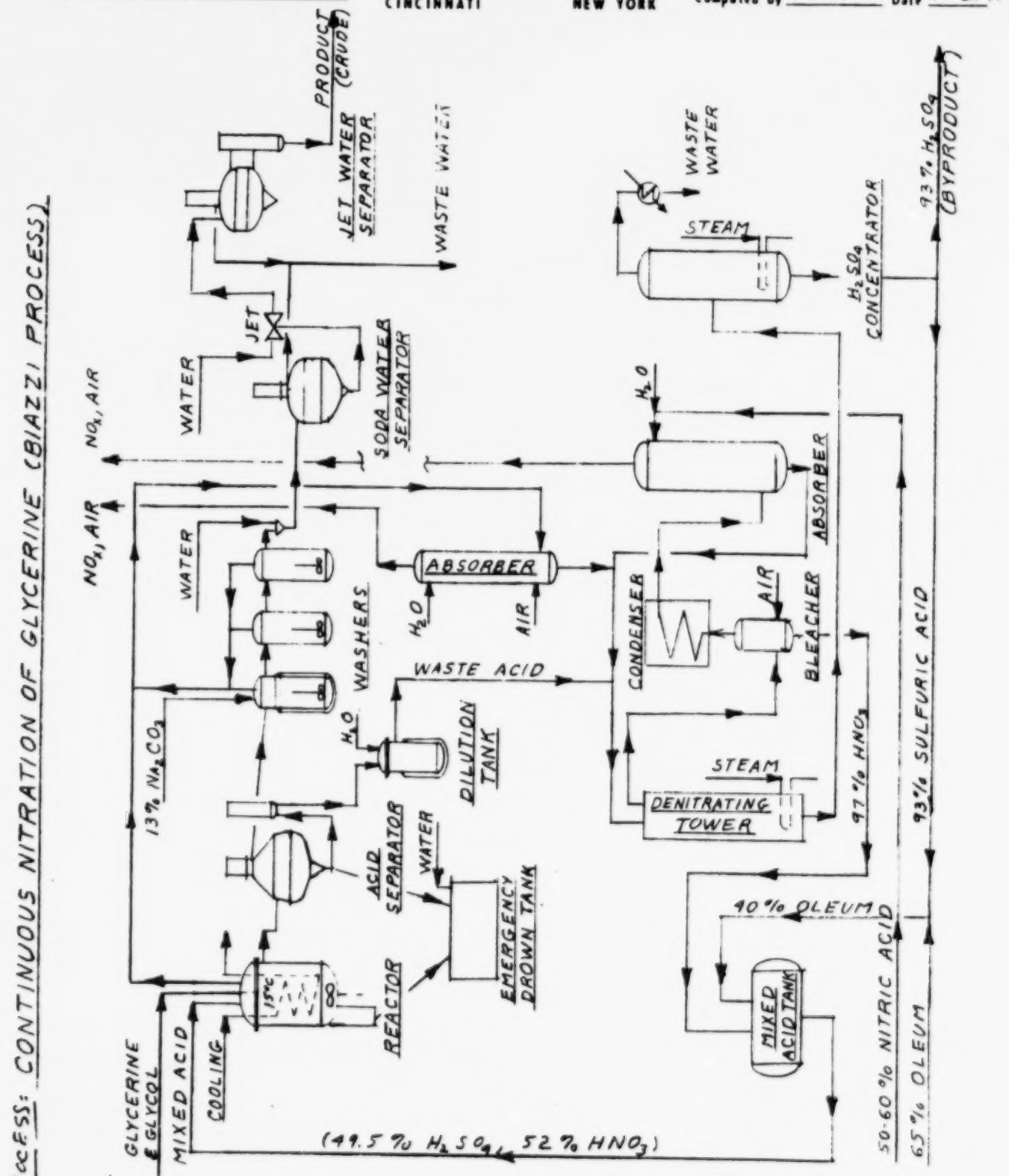
Subject NITRATION STUDY

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

File No 3382 Sheet No

Checked by Date

Computed by G.N.T. Date 10-27-71



PROCESS DATA TABULATION

SH____OF____

SIC. NO.	INDUSTRY	PRODUCT
2892	EXPLOSIVES	NITROGLYCERINE

DATE:	PROCESS
2-28-42	NITRATION OF GLYCERINE

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	9	2
PRODUCT : COLS. 5-8	X		1	3	7
PROCESS : COLS. 9-13				5	5

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
	NO DATA				

COMPUTER CODE NOS.

AQCR 19–22	STATE 23 24	CITY 25–36	COMPANY 37–49	X 50	51	CAPACITY 52–55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2992	EXPLOSIVES	NITROGLYCERINE	SIC. NO. : COLS. 1-4 — X 2 8 9 2
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8 — X 1 3 7
11-15-71	NITRATION OF GLYCERINE	ABSORBER (REACTOR)	PROCESS : COLS. 9-13 — 5 5
			SOURCE : COLS. 14-17 — X 1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	0.6	C

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO (18–20)	CNO (21–23)	UNCON EMISS (24–30)	Q (31)	CEF (32–35)	Q (36)	SCF (37–40)	Q (41)	YR (42)	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

2-42

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2892	EXPLOSIVES	NITROGLYCERINE	SIC. NO. : COLS. 1-4 — X 2892
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8 — X 137
11-15-71	NITRATION OF GLYCERINE	ABSORBER No 2 (ACID RECYCLE)	PROCESS : COLS. 9-13 — 55
			SOURCE : COLS. 14-17 — X 5

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	1.3	C

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO (18 20)	CNO (21 23)	UNCON EMISS (24 30)	Q (31)	CEF (32 35)	Q (36)	SCF (37 40)	Q (41)	YR (42)	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

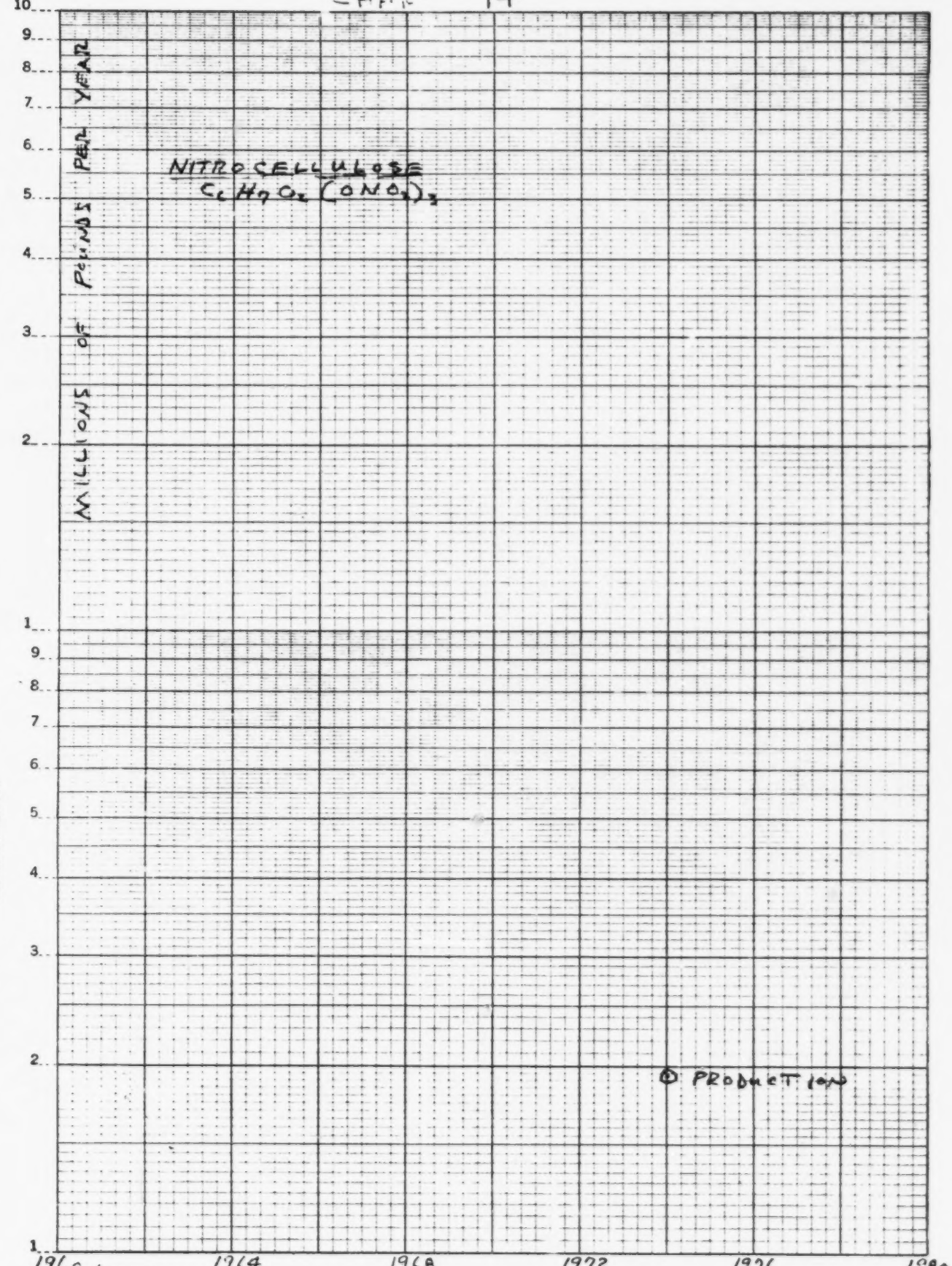
Product: Nitrocellulose

Nitrocellulose is a low explosive which has been in use for over a century. It is produced by nitrating cotton or wood dust,

$$C_6H_7O_2(OH)_3 + 3HONO_2 \longrightarrow C_6H_7O_2(ONO_2)_3 + 3H_2O$$

Nitrocellulose is also used in lacquers, at an average rate of about 1-1/2 million pounds per year. As Chart 14 shows, there is no production data on nitrocellulose.

CHART 14



KE SEMI-LOGARITHMIC 40 485
2 CYCLES X 60 DIVISIONS
KEUFFEL & ESSER CO.

Process: Nitration of Cellulose

a. Feed Preparation

The cellulose is prepared from cotton linters or from specially prepared wood pulp. The starting material is purified for use in nitrating. The cotton linters (or wood pulp) is first boiled with dilute caustic, and then is washed several times with water. This is followed by bleaching several times with bleaching powder or sodium hypochlorite in water. The linters, after drying and loosening, are ready for feed to the reactor.

Mixed acid, with a composition which is approximately 21 percent HNO_3, 63 percent H_2SO_4, 0.5 percent N_2O_4 and 15.5 percent H_2O, is prepared by mixing 93 percent H_2SO_4, 50 to 60 percent HNO_3, and 97 percent HNO_3.

The nitrocellulose prepared using the above mixed acid contains 12.6 percent nitrogen and is called pyrocotton. Other grades of nitrocellulose are pyroxylin (with 8 to 12 percent nitrogen) which is prepared by using mixed acid that is weaker in nitric acid than above, and guncotton (with 13 to 14 percent nitrogen) which is made with a stronger acid.

b. Reactor Conditions

The reaction is usually carried out in a du Pont "mechanical dipper" nitrator, which processes 32 pounds of cellulose per batch. This charge of cellulose is mixed with 1500 pounds of mixed acid at 30C for 25 minutes. The entire batch is dropped into a centrifuge where the spent acid is separated from the nitrated cellulose. The spent acid goes to the acid concentration system. The nitrocellulose is dropped from the centrifuge to a flume where it

is flushed with water to the boiling tub. One reason for the small batch size is that the nitrocellulose picks up moisture from the air in the centrifuge. This causes denitrification of the nitrocellulose, with a buildup of heat, and if it is not drowned quickly enough, explosive conditions can occur.

The reactor and the centrifuge are vented to an absorber where any NO is oxidized and absorbed in water to produce a nitric acid solution. This solution goes to acid concentration.

c. Product Purification

The nitrocellulose in the boiling tub is washed several times with hot water. It is then transferred to a beater, where it is treated with dilute sodium carbonate. It is then washed several times with boiling water and with cold water. The nitrocellulose is then centrifuged to remove excess water. The product nitrocellulose, which contains 23 percent water, is stored wet until it is processed either to explosives or to celluloid or lacquers.

d. Recycle Systems

The acid concentration system is the only recycle system. The spent acid from the centrifuge and the nitric acid from the absorber are fed to the top of the denitrating tower. This tower is heated with steam. As the dilute acids flow down through the tower, the rising vapors strip out oxides of nitrogen and HNO_3. These pass overhead to the bleacher. The water is held in the denitrating tower by the sulfuric acid. The mixture passes out of the bottom of the tower.

The dilute sulfuric acid is then fed to a sulfuric acid concentrator where the water is removed as a waste material. The concentrator produces 93 percent sulfuric acid which is recycled to the mixed acid system.

In the bleacher any NO in overheads from the denitrating tower is oxidized with air. The gases then pass through a reflux condenser where HNO_3 condenses out and drops back to the bleacher. A 97 percent nitric acid solution is withdrawn from the bleacher and goes to the mixed acid system.

The vent gases from the reflux condenser go to an absorber, where further oxidation of NO takes place and the oxides of nitrogen are absorbed in nitric acid and water. Dilute nitric acid is removed from the bottom of the absorber and is recycled to the denitrating tower. Air is vented from the top of the absorber.

e. Raw Materials

The major raw materials are cotton linters or specially prepared wood pulp and 50 to 60 percent nitric acid. Other raw materials are 93 percent sulfuric acid to make up for process losses, calcium or sodium hypochlorite which is used in the cellulose bleaching and sodium hydroxide and sodium carbonate.

f. By-products

There are usually no by-products. Some plants sell the spent acid, instead of concentrating it.

g. Sources of Air Pollution

There are two major sources of possible air pollution. These are the vents from the absorber in the reactor section and the absorber in the acid concentration section. These vents contain air and any unabsorbed oxides of nitrogen. Another pollution source could be the boiling tub, where steam and acid vapors are vented.

PR 109

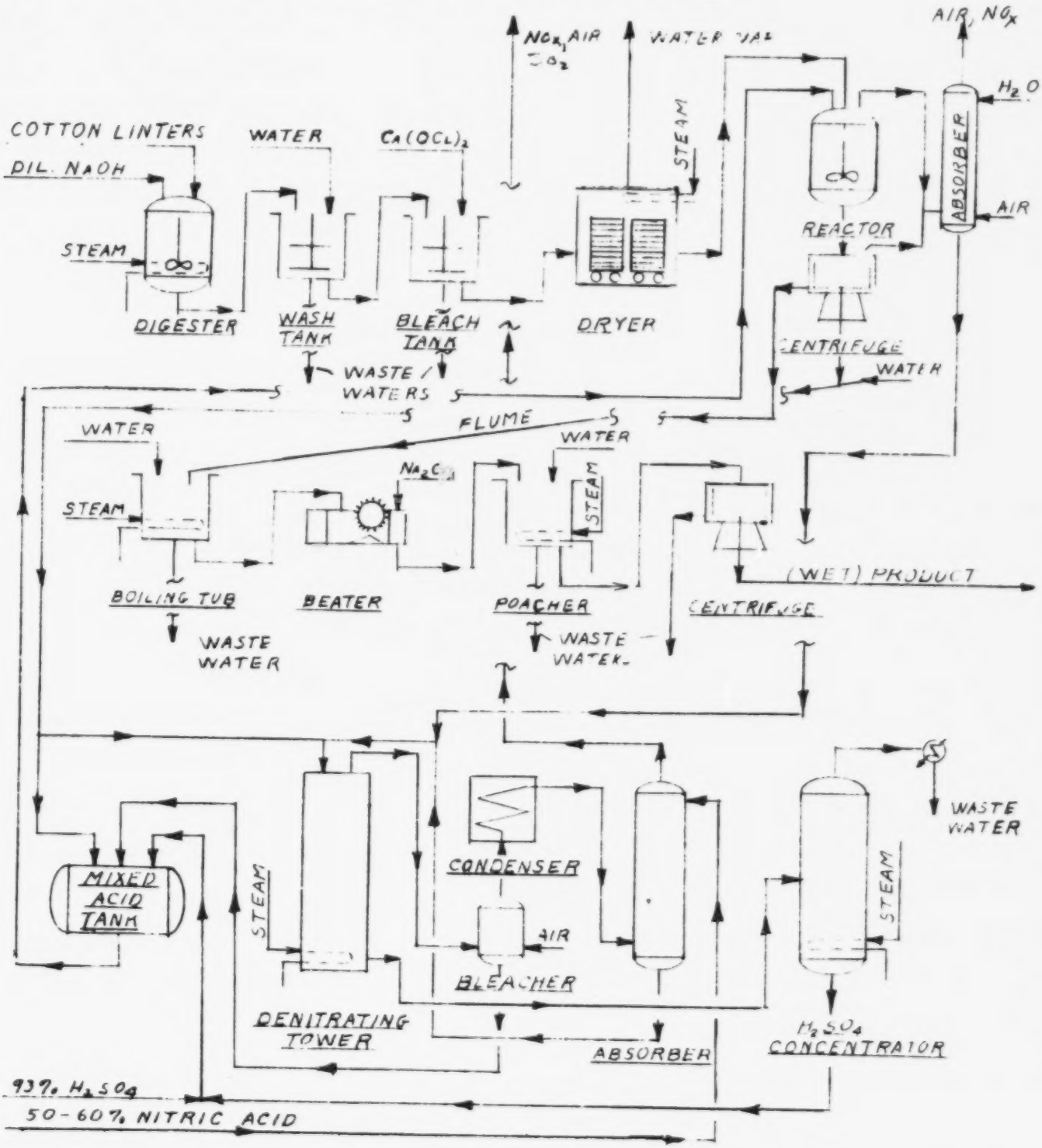
FLOW DIAGRAM
NITROCELLULOSE MANUFACTURE

Job EPA — **PROCESSES RESEARCH, INC.** — File No 3382 Sheet No ____

Location ____ — INDUSTRIAL PLANNING AND RESEARCH — Checked by ____ Date ____

Subject NITRATION STUDY — CINCINNATI NEW YORK — Computed by G N T Date 10-27-71

PROCESS: NITRATION OF CELLULOSE



Q-6

PROCESS DATA TABULATION

SH 1 OF 1

SIC. NO.	INDUSTRY	PRODUCT
2892	EXPLOSIVES	NITROCELLULOSE

DATE:	PROCESS
11-15-71	NITRATION OF CELLULOSE

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	9	2
PRODUCT : COLS. 5-8	X		1	3	8
PROCESS : COLS. 9-13				5	6

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
	(NO DATA AVAILABLE)				

COMPUTER CODE NOS.

AQCR 19–22	STATE 23–24	CITY 25–36	COMPANY 37–49	X 50	CAPACITY 51–55	Q 56	YEAR 57–58

MISCELLANEOUS

RELATED SIC. NOS:

SOURCE DATA TABULATION

1.02

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2892	EXPLOSIVES	NITROCELLULOSE	SIC. NO. : COLS. 1-4 — X 2 8 9 2
DATE PREPARED	PROCESS NITRATION OF CELLULOSE	SOURCE ABSORBER (REACTOR)	PRODUCT : COLS. 5-8 — X 1 3 8
11-15-71			PROCESS : COLS. 9-13 — 5 6
			SOURCE : COLS. 14-17 — X 1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	12	B

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO (18 20)	CNO (21 23)	UNCON EMISS (24 30)	Q (31)	CEF (32 35)	Q (36)	SCF (37 40)	Q (41)	YR (42)	DATE ISS.	REV. NO.	REV. DATE

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

2.0.2

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.					
2892	EXPLOSIVES	NITROCELLULOSE	SIC. NO. : COLS. 1-4	X	2	8	9	2
DATE PREPARED	PROCESS NITRATION	SOURCE	PRODUCT : COLS. 5-8	X		1	3	8
11-15-71	OF CELLULOSE	ABSORBER NO. 2 (ACID RECYCLE)	PROCESS : COLS. 9-13				5	6
			SOURCE : COLS. 14-17	X				5

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	29	B
SO_2	65	B

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				
"				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE	

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

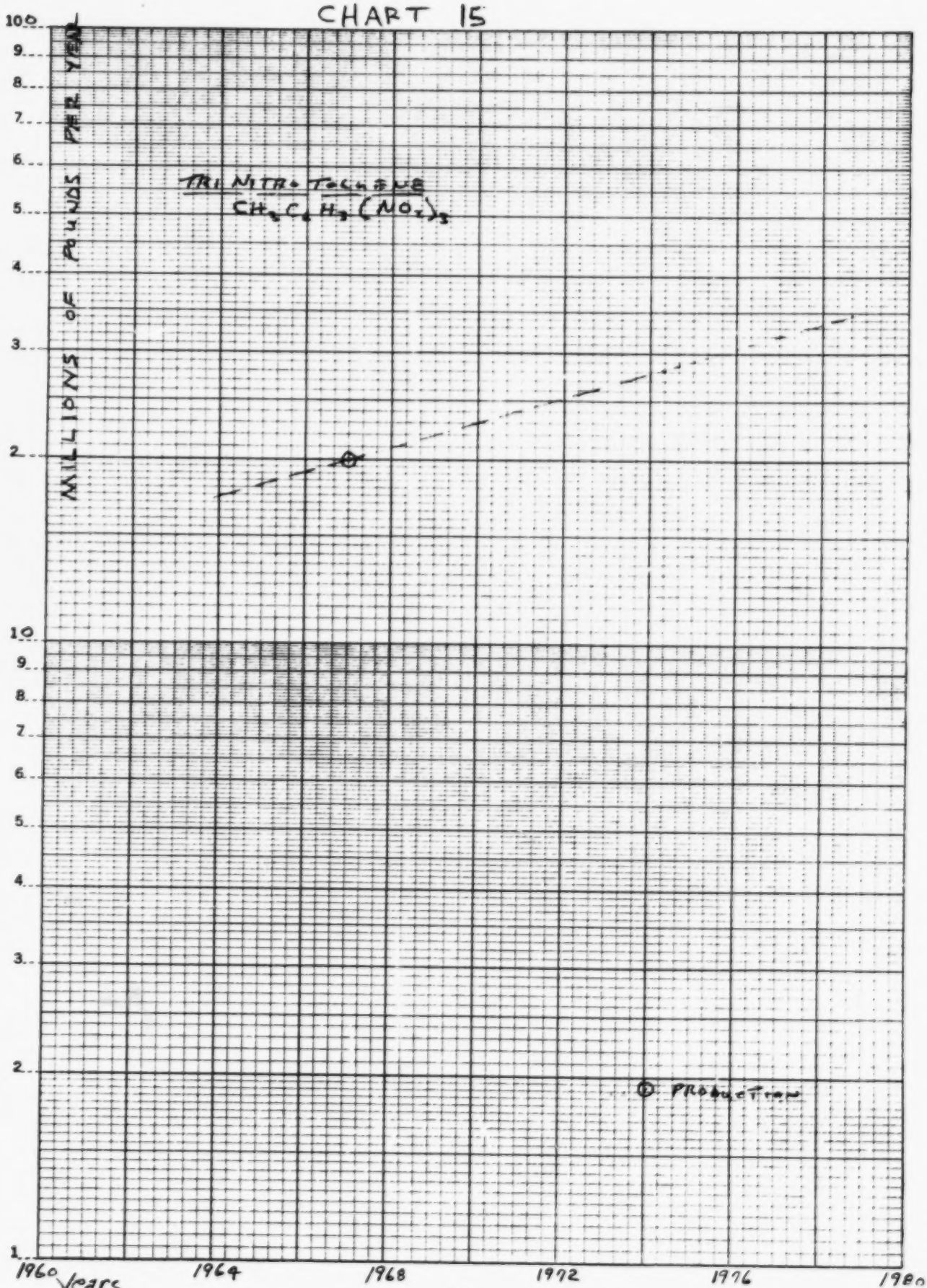
Product: Trinitrotoluene

Trinitrotoluene, TNT, is a high explosive which was first used in World War I. Its only use is as an explosive. Chart 15 shows the single industrial production figure. The reaction is,

$$C_6H_5CH_3 + 3HONO_3 \longrightarrow C_6H_2CH_3(NO_2)_3 + 3H_2O$$

As indicated in the first section, industrial explosives have an estimated annual growth rate of about 6 percent.

CHART 15


MILLIONS OF POUNDS PER YEAR
100
9
8
7
6
5
4
3
2
10
9
8
7
6
5
4
3
2
1
TRINITROTOLUENE
$CH_3C_6H_2(NO_2)_3$
PRODUCTION
1960
1964
1968
1972
1976
1980
years

Process: Nitration of Toluene to Trinitrotoluene

a. Feed Preparation

A mixed acid, which has a composition of 83 percent total sulfuric acid and 23 percent nitric acid is prepared by mixing oleum with a "semi-mix" acid containing 62 percent total sulfuric acid and 43 percent nitric acid. The mixed acid above is called a "tri-mix" acid.

b. Reaction Conditions

The reaction of toluene with nitric acid to produce trinitrotoluene is usually in three steps, each carried out in a separate building as a safety measure. In the first step, mononitrotoluene is produced. The crude nitrotoluene from the first step is nitrated to dinitrotoluene in the second step; in the third step, the dinitrotoluene crude from the second step is nitrated to trinitrotoluene.

Each step of the reaction process consists of one or more nitration reactors piped in series and followed by a separator, such as a decanter or a centrifuge, to separate the crude nitrotoluenes produced from the spent acid. The mixed acid and the toluene or nitrotoluenes flow cocurrently through each step until separated, and counter-current between steps. The reaction conditions are different in each step. Each reactor system is vented to a fume scrubber.

The "tri-mix" acid (discussed under feed preparation) is fed to the third reaction step in the process. The third step reactors operate at 80 to 110C and atmospheric pressure. The ratio of "tri-mix" acid to crude

dinitrotoluene which is fed to the third step reaction is such that little or no excess nitric acid remains in the spent acid.

The spent acid from the third step nitration is fortified with 50 to 60 percent nitric acid. This fortified acid, called "bi-mix" acid, is used in the second reaction step. The "bi-mix" acid has a composition of 54 percent sulfuric acid, 13 percent nitric acid, 17 percent nitrosylsulfuric acid, 8 percent water and 8 percent nitro compounds. The reaction is controlled at 75 to 85C and is at atmospheric pressure.

The spent acid from the second step reaction is fortified with 50 to 60 percent nitric acid to give a "mono-mix" acid with a composition of 48 percent sulfuric acid, 14 percent nitric acid, 17 percent nitrosylsulfuric acid, 19 percent water and 2 percent nitro compounds. This acid is used in the first stage reaction. The reaction conditions are 40 to 55C and atmospheric pressure.

The spent acid from the first step reaction goes to the denitrating tower in the acid concentration section. (See recycle systems.)

c. Product Purification

The crude trinitrotoluene from the third stage reaction system is purified in a series of washing and neutralization steps. The wash water flows counter-current to the nitrotoluene between steps. In the Meissner process the washers are columns in which the nitrotoluene and wash water are fed to the bottom and flow out of the top to a separator. The nitrotoluene layer from the separator goes to the next column while the water layer goes to

the column of the previous step. The wash water from the first step is a waste product. The trinitrotoluene from the last separator is product.

Each wash column is agitated by air which is sparged into the bottom of the column and vented at the top of the column.

The usual wash sequence consists of four treatments. The crude trinitrotoluene is first washed with one or more water washes. This is followed by a dilute caustic wash using sodium bicarbonate to neutralize any inorganic acids. The crude is then treated with sodium sulfite. This reacts with any unsymmetrical trinitrotoluenes and makes them soluble in water. The crude is finally given one or more water washes.

The trinitrotoluene from the last washing step is the product for use in making dynamites.

d. Recycle Systems

There is one recycle system. The spent acid from the first reaction is fed to the top of the denitrating tower. This tower is heated by steam in the bottom. The rising vapors strip the HNO_3 and oxides of nitrogen from the liquid. These nitrogen compounds pass out the top to the bleacher. The water is retained by the H_2SO_4 and flows out the bottom of the tower and then to the H_2SO_4 concentrator.

The nitrogen compounds from the denitrating tower are mixed with air in the bleacher. This converts NO to NO_2. The gases rise through the bleacher and pass through a reflux condenser. This condenses nitric acid with a concentration of 97 percent HNO_3. The acid flows back through the

bleacher absorbing NO_2 and forming more nitric acid. The concentrated nitric acid is withdrawn from the bleacher for use in the semi-mix acid (discussed under feed preparation). The gases that leave the reflux condenser go to an absorption system, consisting of one or more columns. The gases enter the bottom and flow upward, counter-current to a flow of dilute nitric acid. Further oxidation of NO occurs in the absorbers, and additional nitric acid is formed. This acid is fed to the denitrating tower to be concentrated. The absorption system is vented.

The water and sulfuric acid from the bottom of the denitrating tower is concentrated to 93 percent H_2SO_4 in the H_2SO_4 concentrator. The water removed is a waste product while the 93 percent sulfuric acid produced goes partly to the semi-mix acid and that portion which cannot be used for semi-mix acid is a by-product.

e. Raw Materials

The major raw materials used in the process are toluene, 50 to 60 percent nitric acid and oleum. Minor raw materials are caustic, sodium bicarbonate and sodium sulfite.

f. By-products

One by-product is produced, the 93 percent sulfuric acid. It contains nitrobodies which limit its marketability.

g. Sources of Air Pollution

There are about eight vents on the process. Three of the vents are on the three scrubbers associated with the three reaction steps. These

will vent any oxides of nitrogen from the reactors that were not absorbed in the scrubbers. Four (or more) vents are on the product washing columns. These will vent air saturated with water and nitrotoluenes. The last vent is the vent from the absorber in the acid concentration section. This vent is mainly air. It will also contain some oxides of nitrogen and HNO_3 fumes.

PR 109

FLOW DIAGRAM
TRINITROTOLUENE MANUFACTURE

Job E. P. A.

Location

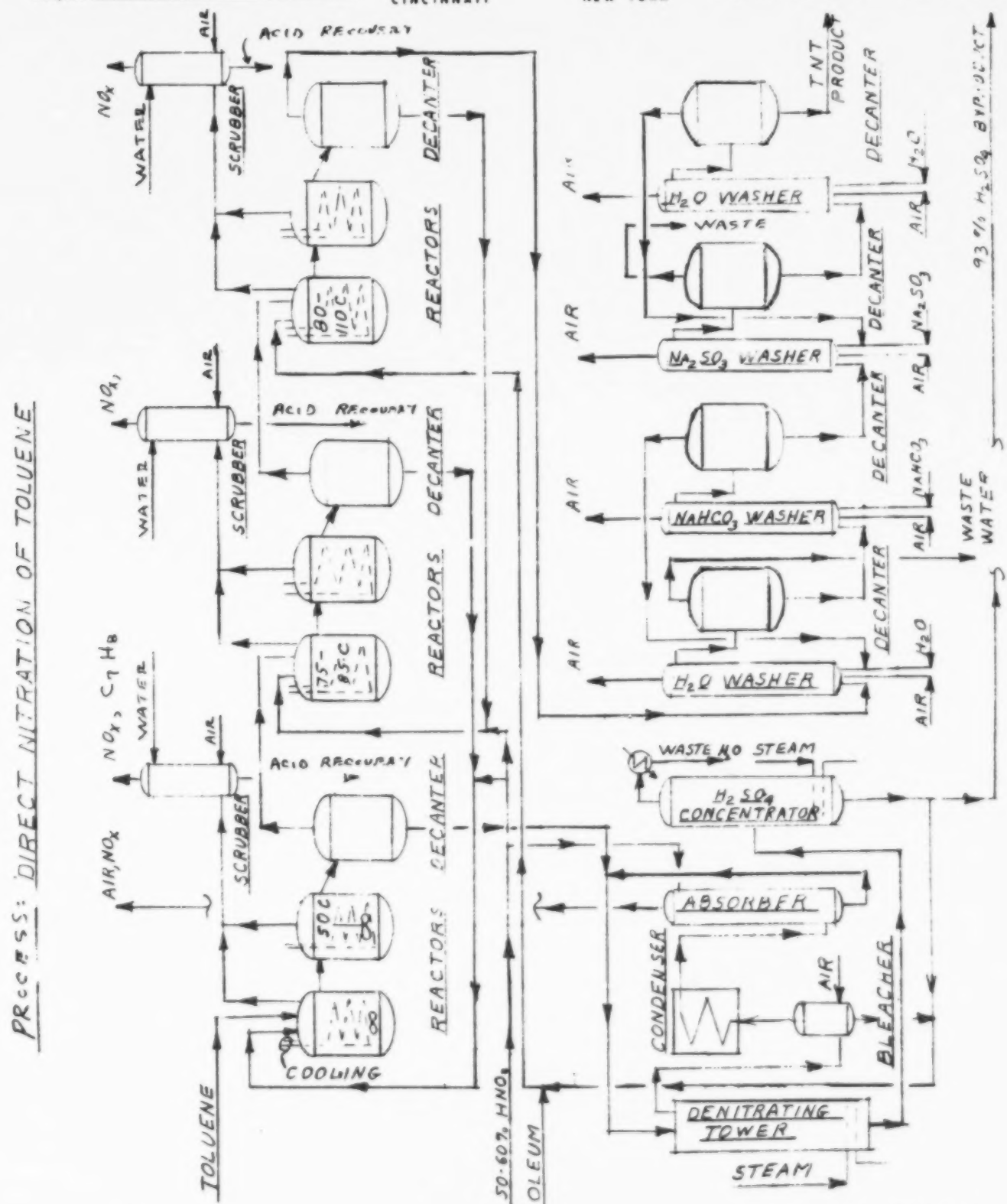
Subject NITRATION STUDY

PROCESSES RESEARCH, INC.
INDUSTRIAL PLANNING AND RESEARCH
CINCINNATI NEW YORK

File No 3382 Sheet No

Checked by Date

Computed by GNT Date 10-28-71



Q: 1

PROCESS DATA TABULATION

SH____OF____

SIC. NO.	INDUSTRY	PRODUCT
2892	EXPLOSIVES	TRINITROTOLUENE

DATE:	PROCESS
11-16-71	NITRATION OF TOLUENE

COMPUTER CODE NOS.

SIC. NO. : COLS. 1-4	X	2	8	9	2
PRODUCT : COLS. 5-8	X		1	3	9
PROCESS : COLS. 9-13				5	7

PRODUCTION DATA

AQCR	COMPANY	LOCATION	Q_1	PRODUCTION	Q_2
	NO DATA	AVAILABLE			

COMPUTER CODE NOS.

AQCR 19–22	STATE 23 24	CITY 25–36	COMPANY 37–48	X 49	CAPACITY 50 61 62–55	Q 56	YEAR 57 58

MISCELLANEOUS

RELATED SIC. NOS.

SOURCE DATA TABULATION

1 of 3

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2892	EXPLOSIVES	TRINITRO TOLUENE	SIC. NO. : COLS. 1-4 — X 2 8 9 2
DATE PREPARED	PROCESS NITRATION OF TOLUENE	SOURCE	PRODUCT : COLS. 5-8 — X 1 3 9
11-16-71		REACTORS	PROCESS : COLS. 9-13 — 5 7
			SOURCE : COLS. 14-17 — X 3 0

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	5	A
$C_7 H_8$	27	
MNT	NIL	A
DNT	NIL	A
TNT	NIL	A

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				
"				
"				
"				
"				

COMPUTER CODE NOS.

PNO 18 20	CNO 21 23	UNCON EMISS 24 30	Q 31	CEF 32 35	Q 36	SCF 37 40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE	

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

2.03

INDUSTRY NO.	INDUSTRY	PRODUCT	COMPUTER CODE NOS.
2892	EXPLOSIVES	TRINITROTOLUENE	SIC. NO. : COLS. 1-4 — X 2 8 9 2
DATE PREPARED	PROCESS	SOURCE	PRODUCT : COLS. 5-8 — X 1 3 9
11-16-71	NITRATION OF TOLUENE	WASHERS	PROCESS : COLS. 9-13 — 5 7
			SOURCE : COLS. 14-17 — X 4 4

POLLUTANT / CONTROL DEVICE

DESCRIPTION	EMISSION FACTOR	Q	TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NO_x	NIL	A	NONE				
TNT	NIL	A	"				
SO_2	NIL	A	"				

COMPUTER CODE NOS.

PNO 18–20	CNO 21–23	UNCON EMISS 24–30	Q 31	CEF 32–35	Q 36	BCF 37–40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE	

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

SOURCE DATA TABULATION

3-03

INDUSTRY NO.	INDUSTRY	PRODUCT
2892	EXPLOSIVES	TRINITROTOLUENE
DATE PREPARED	PROCESS	SOURCE
11-16-71	NITRATION OF TOLUENE	ABSORBER (HNO_3 RECYCLE)

COMPUTER CODE NOS.

	COLS.				
SIC. NO.	1-4	X	2	8	9	2
PRODUCT	5-8	X		1	3	9
PROCESS	9-13				5	7
SOURCE	14-17	X				1

POLLUTANT

DESCRIPTION	EMISSION FACTOR	Q
NO_x	12	A

CONTROL DEVICE

TYPE	EFF. FACTOR	Q	SOURCE FACTOR	Q
NONE				

COMPUTER CODE NOS.

PNO 18-20	CNO 21-23	UNCON EMISS 24-30	Q 31	CEF 32-35	Q 36	SCF 37-40	Q 41	YR 42	DATE ISS.	REV. NO.	REV. DATE	

FOR PRODUCTION CAPACITIES SEE PRODUCTION LISTING _____

RELATED INDUSTRIES

BIBLIOGRAPHY

D. AIR POLLUTION CONTROL DEVICES OF NITRIC ACID PLANTS

1. Process Description

Over 95 percent of the nitric acid is produced by the high pressure air oxidation of ammonia,

$$NH_3 + 2O_2 \underset{(Air)}{} \xrightarrow[900C]{135\ psia} HNO_3 + H_2O$$

There are two other processes, low pressure air oxidation and the Hoko, neither of which are used in the United States.

The absorber tower is the last piece of equipment in the nitric acid process train. The vent from the absorber tower usually contains 3000 ppm of NO_x, half as NO and half as NO_2. The main component of the vent is nitrogen, along with 1 to 5 percent oxygen.

2. Control Devices

In the United States the most widely used control device on the gaseous effluent from the nitric acid absorber is a one-or two-stage non-selective catalytic reducer. In the first stage, the NO_2 and oxygen are reduced by fuel gas (methane) to carbon dioxide, water, and nitric oxide. After the effluent is cooled, the nitric oxide is reduced in the second stage with additional fuel gas to nitrogen, water, and carbon dioxide. If the effluent from the absorber has a low oxygen content, say less than 2 percent, then a single stage catalytic reducer is used as a control device. The nitric oxide content of the effluent from the catalytic reducers can be controlled down to less than 50 ppm, but efficiency factors average 80 percent. The unit is considered flexible and adequate. Caustic scrubbers are used to a very minor extent as

control devices on nitric acid plant absorbers. Caustic scrubbers produce sodium nitrate, a solids disposal problem. Catalytic reducers produce the natural components of air. The efficiency factors of caustic scrubbers average 90 percent.

3. Utilization

a. Catalytic Reducers

It is thought that catalytic reducers of nitric acid plants could be used effectively on these five nitro processes.

Nitration of benzene
Oxalic acid by the oxidation of monosaccarides
Nitration of toluene to trinitrotoluene
Nitroparaffins from propane
Dinitrotoluene

The vents from these flue processes are dilute streams of NO_x. The streams also contain hydrocarbons which would compliment the added fuel (methane).

b. Scrubbers

Where particulate is the main emission, water or alkali scrubbers would be effective with these four processes:

Ammonium nitrate prills
Ammonium nitrate granules
Sodium nitrite
Potassium nitrate

Caustic scrubbers would also be effective with these two nitro processes:

Nitration of glycerine
Nitration of cellulose

The remaining four nitro processes will require the development of different types of control devices.

SECTION III - CONCLUSIONS

A. POLLUTION BY PROCESSES

In Table 3 the four classes of processes have been listed according to their percentage of total pollutant emission based on total product capacity and emission factors. The liquid phase nitric acid oxidations, Class 3, is the largest polluting class of processes, emitting about half the air pollutants while consuming only about one eighth of the total nitric acid production.

TABLE 3 - POLLUTION BY PROCESSES

Process Description	Process Classification Number	Percent of Total Pollution Emissions	Percent of Nitric Acid Consumption
Liquid phase nitric acid oxidations	3	52	12
Nitric oxide oxidations	4	1	2
Vapor phase nitrations	2	13	8
Liquid phase nitrations	1	34	72

For the Nineteen-seventies, it is expected that only minor changes will occur in the above figures. It is expected that ammonium nitrate production will continue to dominate nitric acid utilization, which is a major factor affecting the above.

In general, nitro processes are not significant polluters, accounting for only 0.06 percent of the total emissions of oxides of nitrogen to the atmosphere. Their significance is important as local source pollution.

B. CONTROL DEVICES

1. Catalytic Reducer

As discussed in Section II D the major control device incorporated in nitric acid plants is a nonselective catalytic reducer. This control device probably can be utilized on the following nitro processes:

Process Class	Product	Major Pollutant	Total Uncontrolled Emission Rate Pounds/Ton of Product
1	Nitrobenzene	Organic	17.1
1	Dinitrotoluene	NO_x	0.27
1	Trinitrotoluene	Organic	44
2	Nitroparaffins	NO_x	1.5
3	Oxalic acid	NO_x	6.3

2. Caustic Scrubber

To a minor extent, caustic scrubbers are control devices for nitric acid plants. Caustic scrubbers would be effective control devices on these two nitro processes:

Process Class	Product	Major Pollutant	Total Uncontrolled Emission Rate Pounds/Ton of Product
1	Nitroglycerine	NO_x	1.9
1	Nitrocellulose	SO_2	96

3. Other Types of Control Devices

For the remaining nitro processes, the following control devices probably would be effective:

Process Class	Product	Major Pollutant	Total Uncontrolled Emission Rate Pounds/Ton of Product
a. Water Scrubbers			
1	Ammonium nitrate prills	Particulate	0.86
2	Ammonium nitrate granules	Particulate	5.5
3	Potassium nitrate and chlorine	Particulate	13
4	Sodium nitrite	Particulate	1.8
b. Two-Stage Caustic Oxidizing Scrubber			
3	Adipic acid	(N_2O)	14
3	Terephthalic acid	(N_2O)	15
c. Vent Condenser			
1	Nitrochlorobenzene	Chlorobenzene	4.1
d. Flare			
4	Acrylonitrile	Organic	5.4

The bottoms from the water scrubbers can be recycled, eliminating the problem of disposing of the solute.

For the emissions from the adipic acid and terephthalic acid processes, the standard catalytic reducers cannot be utilized because of the high N_2O content which will react with the fuel, causing high fuel consumption and high temperatures. The two-stage caustic scrubber must be oxidizing (air present) in nature in order to maintain the optimum NO/NO_2 ratio for efficient absorption.

Due to the chlorine content in the effluent from the nitrochlorobenzene process, the catalytic reducers and caustic scrubbers will not be effective as control devices. It is expected that a vent condenser would be most effective control device.

For control devices on the air effluents from acrylonitrile plants using the NO/propylene process, a flare would be satisfactory since the main component of the effluent is hydrocarbons.

C. INSTRUMENTATION

Adequate instrumentation for process control of nitro processes and for the utilization of pollution control devices is currently applied for process plants.

D. UPSETS

Although process upsets, when the reaction gets out of control, are outside the scope of this study, certain items should be noted.

The liquid phase nitration processes, Class 1, are the most serious source of air pollution from process upsets. Up to the present time, minor development of control devices for such processes has been done.

E. INCENTIVES FOR CONTROL OF EMISSIONS

At a cost of 4 cents per pound, the recovery of nitric acid and the oxides of nitrogen (NO_x) can be economically done. This is a significant incentive to minimize atmospheric emissions.

The oxides of nitrogen have undesirable physiological effects, but are not really hazardous. Therefore, this is a weak incentive.

Concentrations of NO_x from chemical process sources are readily visible as a brown-red gas. Therefore, this is a strong incentive to reduce the plume and its connotation of pollution.

F. ADSORPTION

Due to the presence of water vapor in the air effluent from most nitro processes, development work on adsorbents would not be productive. Furthermore, the NO_x level desired in the exit gases from adsorbent bed control devices appears to be beyond the effective limit achievable by most adsorbents.

G. SIZE FACTOR

Other than ammonium nitrate and adipic acid, and possibly terephthalic acid, acrylonitrile, nitrobenzene, and dinitrotoluene, the production of nitro products is small compared, say, to the chloro products. Even with growth of the industry and the development of continuous process trains, control will continue to be most important on a local source basis with local economical conditions governing.

SECTION IV - RECOMMENDATIONS

A. ADAPTATION OF EXISTING CONTROL DEVICES

It is recommended these existing control devices can be adapted for use on these nitro processes where local source conditions require control device utilization.

Control Device	Product	Process
1. Nonselective catalytic reducers	Nitrobenzene	Nitration of benzene
	Dinitrotoluene	Nitration of toluene
	Trinitrotoluene	Nitration of toluene
	Nitroparaffins	Nitration of paraffins
	Oxalic acid	Oxidation of monosaccharides
2. Caustic scrubbers	Nitroglycerine	Nitration of glycerine
	Nitrocellulose	Nitration of cellulose
3. Water Scrubbers	Ammonium nitrate prills	Nitration of ammonia
	Ammonium nitrate granules	Nitration of ammonia
	Potassium nitrate	Oxidation of potassium chloride
	Sodium nitrite	Oxidation of sodium carbonate
4. Flare	Acrylonitrile	NO - propylene
5. Vent condenser	Nitrochlorobenzene	Nitration of chlorobenzene

B. DEVELOPMENT OF NEW CONTROL DEVICES

For some of the Class 3 type of processes, nitric acid oxidation, it is recommended that an improved design for oxidizing caustic scrubber be developed as a control device. To be more effective, the scrubber should be selective for NO/NO_2 mixtures. When further developed, the control device could be used on the nitro processes of adipic acid and terephthalic acid.

C. PROCESS UPSETS

It is recommended that development work be done on confining the vapors from a drown tank, when a nitration reactor is dumped. Vapors should be collected and fed to a caustic scrubber before being allowed to vent to the atmosphere.

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